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TEXTILE RESEARCH JOURNAL

VOL. XXVI, NO. 4 APRIL 1956

The Reversible Effect of Temperature on the Mechanical Properties of Tire Yarns and Cords

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1. Introduction

The main purpose of a tire cord is to give strength and dimensional stability to the rubber. Therefore, among other properties, a tire cord must possess a high strength, and its growth must not be excessive. It must also be able to withstand for a considerable period the severe flexure which occurs in service.

The mechanical properties of textiles are affected by temperature and humidity. The continual flexing of the rubber causes the generation of a considerable amount of heat, thereby increasing the temperature of the tire. With the high road speeds encountered today, the temperature may rise as high as 120° C. in the case of heavy duty tires. It has been shown that moisture diffuses more rapidly through hot rubber than through cold. Consequently, there is a greater tendency for moisture to leave the fabric when the tire is in service, than for the converse effect when the tire is standing at normal temperature. In other words, because of this differential diffusion of the moisture through the rubber when the temperature is raised, the moisture content of the textile in a tire under normal service conditions is usually much less than would be the case if the fabric were in equilibrium with the surrounding atmosphere. The properties of the fabric in the hot, bone-dry state are consequently of greater importance than those in the normal conditioned state.

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2. The Effect of Temperature on Tensile Strength and Extensibility

2.1 Reversible and Irreversible Effects

The effects of temperature on the strength of textiles may be classified as the reversible and irreversible effects. Up to a certain limit, an increase in temperature causes a decrease in strength, the original strength being regained on cooling, providing that the textile is not maintained at an elevated temperature for too long a period. This is referred to as the reversible effect.

Prolonged exposure of a textile at elevated temperature may lead to a permanent drop in strength. This is the irreversible effect, and its magnitude is dependent on the nature of the environment as well as on the temperature and the time of heating. This paper is concerned with the reversible effect only.

2.2 Tensile Testing of Yarns and Cords at Elevated Temperatures

The reversible effect of temperature on strength and extensibility may be conveniently investigated using conventional tensile testing apparatus provided with a heating chamber to accommodate the yarns or cords. Dillon and Prettyman [3] have reported some results on the effect of temperature and humidity. These authors employed a pendulum-type textile tester. In the arrangement, however, the ends of the cord became exposed to the atmosphere as the sample extended. This gave rise to a number

of jaw breaks, particularly in the case of rayon cords, the end regions being weakened by the absorption of moisture. Furthermore, the arrangement did not permit an accurate determination of extensibility since the cord was neither at a uniform temperature along its length nor was its regain uniform, owing to the absorption of moisture by the ends of the cord.

Busse, Lessig, Loughborough, and Larrick [1] have published curves showing the variations of the tensile strength of rayon and cotton tire cords with temperature. Here again, the results were rendered somewhat uncertain by a tendency for jaw breaks to occur at the elevated temperatures. Also, since the oven had an absolute moisture content of 65% R.H. at 72° F., the curves show the combined effects of temperature and drying.

In the work carried out by the present authors, a Scott inclined plane textile tester (Model I.P.4) was employed. This was equipped with a hot box, so designed that the cord or yarn to be tested was totally enclosed throughout the test.

If, using a Scott I.P.4 tester, the yarn is to remain enclosed within the heated chamber during a test, then the rod attaching the jaw to the load carriage must be extended so that the movement of this jaw is always confined to the interior of the hot box. The arrangement is shown schematically in Figure 1. No complications arise in the case of an I.P.4 tester designed to take 20-in. specimens, but in the case of those testers which take only 10-in. sample lengths, it is necessary to extend the length of the inclined

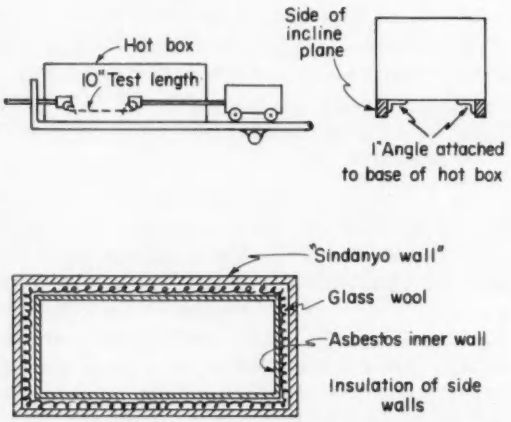

Fig. 1. Schematic arrangement of the hot box on the Scott I.P.4.

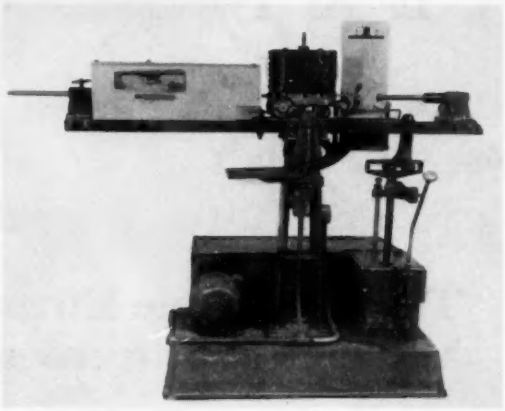

Fig. 2. General view of Scott I.P.4 with hot box attached.

plane so that 10-in. test lengths may be used within the hot box.

Since the hot box is illustrated in Figures 2 through 4, it is unnecessary to give a lengthy description of the apparatus. The walls of the chamber were constructed from ¼-in. "Sindanyo" asbestos board, this material having the advantage of being easily worked. To minimize heat losses, the sides were provided with interior walls of asbestos, and the gap between the two walls was packed with glass wool. The side of the chamber facing the operator was provided with a glass window. Two parallel lengths of 1-in. angle iron attached to the base of the chamber, one on either side, enabled the apparatus to be clamped to the sides of the inclined plane.

It was found convenient to modify the jaws of the Scott so that they could be operated by the screw motion of a key as indicated in Figure 3.

The chamber was heated electrically using two 500-watt asbestos-woven heating mats connected in parallel. These were mounted on the floor of the chamber and covered by a metal gauze to prevent direct contact with the cord. A stream of air from a compressed air supply was introduced into the chamber from one end. By adjusting the tilt of the air inlet and by controlling the rate of flow, it was found possible to maintain a uniform temperature between the two jaws. In the case of bone-dry tests, the air was dried by being passed through an activated alumina drying tower before entering the hot box.

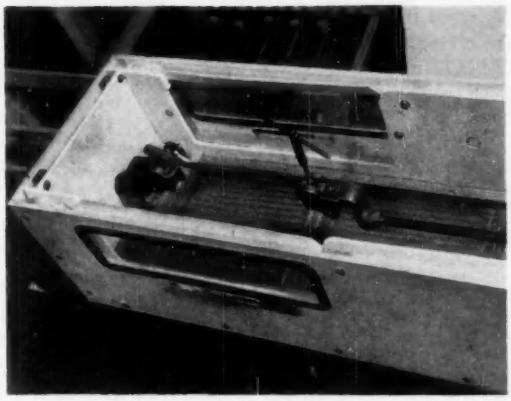

Fig. 3. Interior view of hot box showing key for operating the jaws.

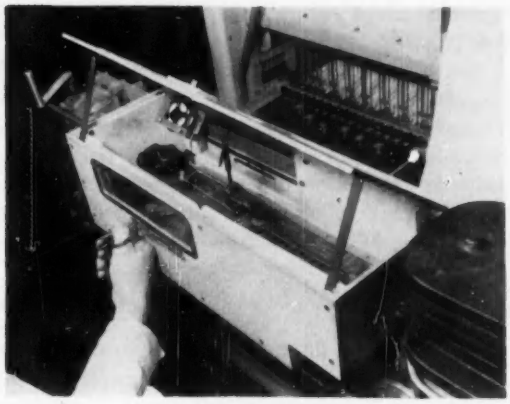

Fig. 4. General view of hot box showing method of manipulating the test yarn.

The length of cord or yarn to be tested was first hanked and allowed to condition for 24 hr. in the standard laboratory atmosphere at 22° C. and 65% R.H. It was then wound onto a typewriter spool under slight tension. This was predried over silica gel for about 24 hr. and then put into an oven and allowed to dry out for an hour at a temperature between 120° and 140° C. This treatment left the yarn in a bone-dry state. It was found preferable to use a spool with cut away sides to permit the rapid escape of moisture from the cord.

The spool was then rapidly transferred from the oven and dropped onto the mounting provided for it in the hot box which was at the desired testing temperature. This mounting (see Figure 3) was provided with rollers which held the spool in place, but also permitted it to rotate freely so that the cord could be pulled off with ease (see Figure 5). A further ¼ hr. was allowed to elapse to ensure that the cord was in equilibrium.

The cord was manipulated inside the chamber by means of a pair of ordinary long-nosed chemical tongs which were introduced through a rectangular slot in the side of the hot box nearest the operator. The operation is clearly shown in Figure 4. Manipulation of the cord became very easy with a little practice.

When the cord had been put around the bollards of the two jaws, the jaw attached to the load carriage was closed. The cord was then tensioned manually and the other jaw closed.

Using the apparatus described above, there was no tendency for an excessive number of jaw breaks to occur at any temperature within the range 20°–160° C.

2.3 The Reversible Effect of Temperature on the Strength and Extensibility of Regenerated Cellulose Yarn

Three different yarns were investigated: (1) 1650-den. continuous-spun viscose, (2) 1180-den. pot-spun rayon, and (3) 1100-den. Fortisan. For each type of yarn, tests were carried out under bone-dry conditions at temperatures starting at 20° C. and increasing by 20° steps to 160° C., the general

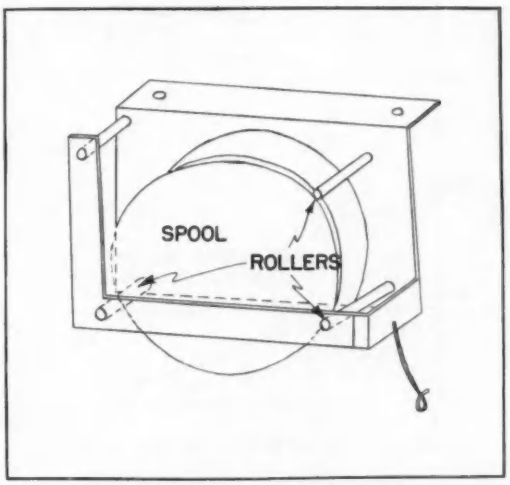

Fig. 5. Diagram of spool holder.

experimental procedure being as described in section 2.2.

Ten individual tests were carried out at each temperature. Eight successive lengths, each comprising ten individual test lengths, were taken from the same cheese of yarn, and the tests were carried out with the temperature arranged in a random order sequence as follows. (Number denotes order in which length was taken from bobbin.)

Test length	1	2	3	4	5	6	7	8
Temperatures, (°C.)	120	40	140	20	60	80	160	100

This was done three times in all so that 30 individual tests were made at each temperature. By adopting this procedure, it was hoped to eliminate both short- and long-range variation of quality throughout the cheese.

The variation of breaking strength in grams per denier (S_B) with temperature for the three types of yarn is shown graphically in Figure 6. For each yarn the breaking strength decreases continuously with increasing temperature. Contrary to the findings of Dillon and Prettyman [3], no minimum was observed in the case of Fortisan. The magnitude of the effect is indicated by the figures in Table I.

TABLE I

Temperature (° C.)	% Drop in strength: 1650-den. viscose	1180-den. viscose	1100-den. Fortisan
20	0	0	0
100	20	17	24.4

If the breaking strength (S_B) is plotted against the reciprocal of the absolute temperature ($1/T°$ K.), as in Figure 7, it would appear that to a first approximation at least, there exists a linear relationship between breaking strength and $1/T$, thus

$$S_B = A + \frac{B}{T} \qquad (1)$$

where A and B are constants for a given yarn. The results of an analysis of variance of the data appear in Tables II through IV. The kilogram unit

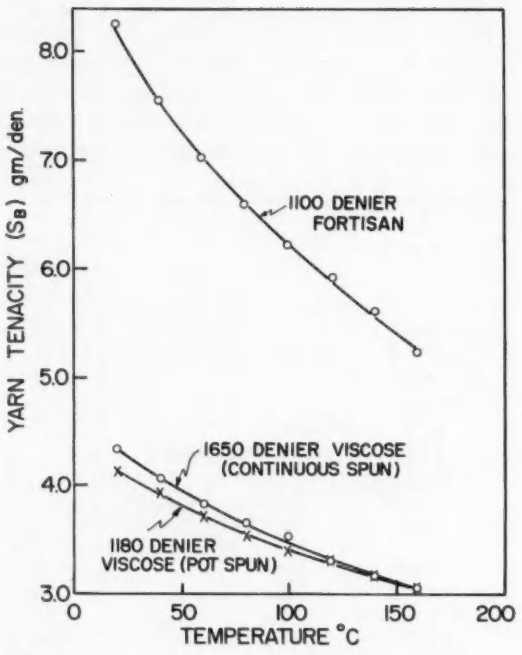

Fig. 6. Variation of yarn tenacity with temperature.

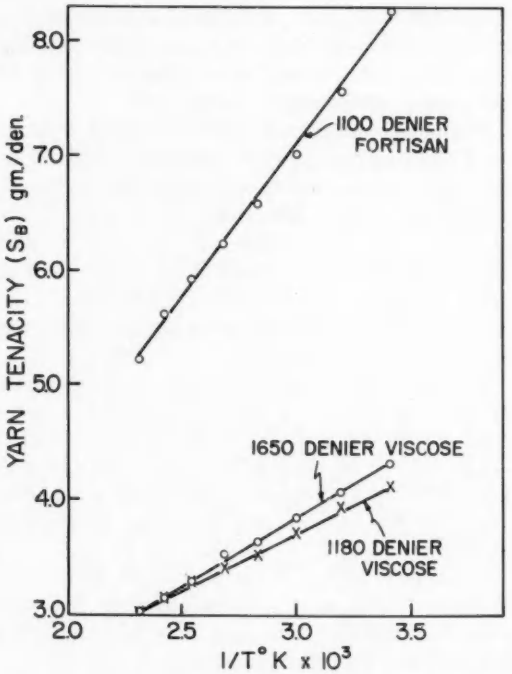

Fig. 7. Yarn tenacity vs. reciprocal of absolute temperature.

TABLE II. 1650-Den. Viscose

Source of variation	Analysis of variance: Sum of squares	Degrees of freedom	Mean square
Regression	119.3	1	119.3
Deviation from regression	0.2712	6	0.0452
Within temperatures (residual)	5.2764	232	0.02274

TABLE III. 1180-Den. Tenasco

Source of variation	Analysis of variance: Sum of squares	Degrees of freedom	Mean square
Regression	41.905	1	41.905
Deviation from regression	0.908	6	0.0163
Within temperatures (residual)	3.363	232	0.0145

TABLE IV. 1100-Den. Fortisan

Source of variation	Analysis of variance: Sum of squares	Degrees of freedom	Mean square
Regression	261.96	1	261.96
Deviation from regression	0.77	6	0.13
Within temperatures (residual)	16.503	232	0.071

was used in the analysis of variance, but the final result is expressed in grams per denier.

Comparison of the regression mean square with the residual mean square shows that the regression line is highly significant. The variance ratio for the deviation from regression is not significant at the 5% level.

The best estimate of the regression coefficient was found to be 1.19×10^3 and the equation of the regression line,

$$S_B \text{ (g./den.)} = 0.246 + \frac{1.19 \times 10^3}{T} \qquad (2)$$

As in the previous case, the regression line is found to be highly significant. The variance ratio for the deviation from regression is not significant at the 5% level. The best estimate of the regression coefficient was found to be 0.98×10^3 and the equation of the regression line,

$$S_B \text{ (g./den.)} = 1.60 + \frac{0.98 \times 10^3}{T} \qquad (3)$$

As before, the regression line is highly significant. The variance ratio for the deviation from regression is not significant at the 5% level.

The best estimate of the regression coefficient was found to be 2.64×10^3 and the equation of the regression line,

$$S_B \text{ (g./den.)} = -8 + \frac{2.64 \times 10^3}{T} \qquad (4)$$

It may be concluded that for each of the three yarns the data are in accordance with a relationship having the form of Equation 1.

The variation of the per cent extensibility at break (E_{Br}) is shown in Figure 8. In the case of the two viscose yarns, the extensibility at break increases with temperature, while with Fortisan, it remains approximately independent of temperature.

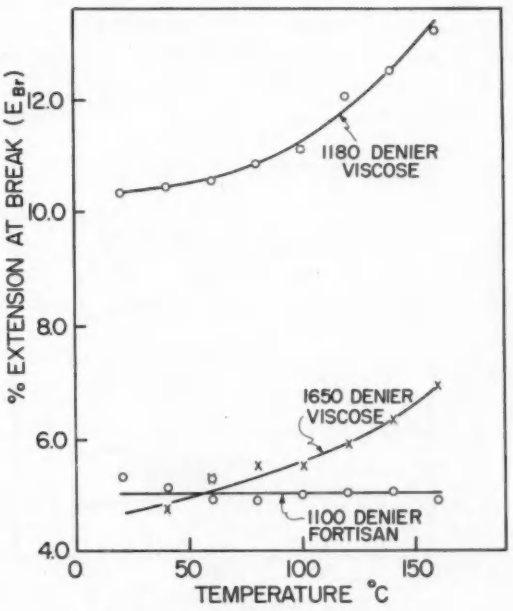

Fig. 8. Variation of yarn extension at break with temperature.

The Scott charts on which the force-extension curves were registered did not permit an accurate determination of the initial modulus for the yarn. Because of this, it was decided to take the ratio of breaking strength to the extension at break, i.e., S_B/E_{Br}, as a measure of the average modulus. The variation of this ratio with temperature is shown in Figure 9. It will be observed that the ratio decreases linearly with temperature. Insofar as this ratio is a measure of the "modulus" of the yarns, the results indicate that the modulus decreases with temperature.

The product $\frac{1}{2}\ S_B \times E_{Br}$ was taken as a measure of the work to rupture. This, of course, is not strictly correct on account of the nonlinearity of the load-extension curves for the yarns studied. However, as an increase in temperature did not produce any marked change in shape of the force-extension curves, it was considered that the variation of this simple product with temperature represented the variation of the work to rupture with temperature.

The product $S_B \times E_{Br}$ is plotted against temperature in Figure 10. This product was very nearly independent of temperature in the case of the viscose yarns. Thus for viscose the increase in extensibility compensates for the decrease in breaking strength. In the case of Fortisan, the extensibility at break was very nearly independent of temperature, and so the decrease of the work to rupture with temperature was a direct consequence of the decrease in breaking strength.

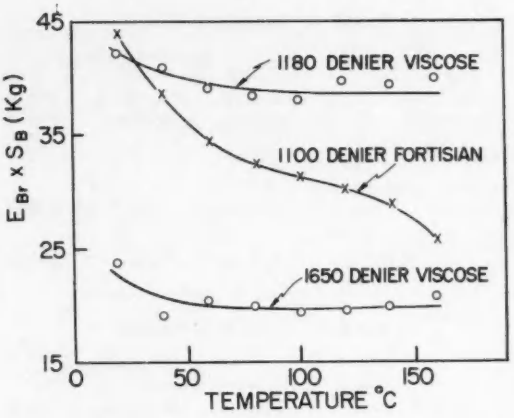

Fig. 10. Variation of yarn breaking strength (kg.) × % extension at break with temperature.

2.4 The Reversible Effect of Temperature on the Strength and Extensibility of Tire Cords

Although it was to be expected that the properties of tire cords would be affected by temperature in the same general way as the yarn, it was thought that an extension of the investigation to cords might be

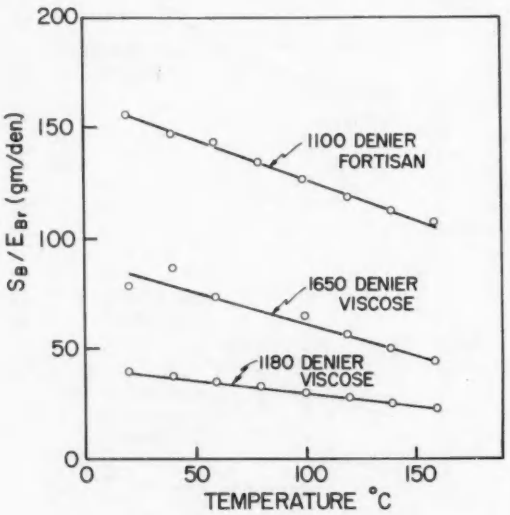

Fig. 9. Variation of yarn tenacity/breaking strain with temperature.

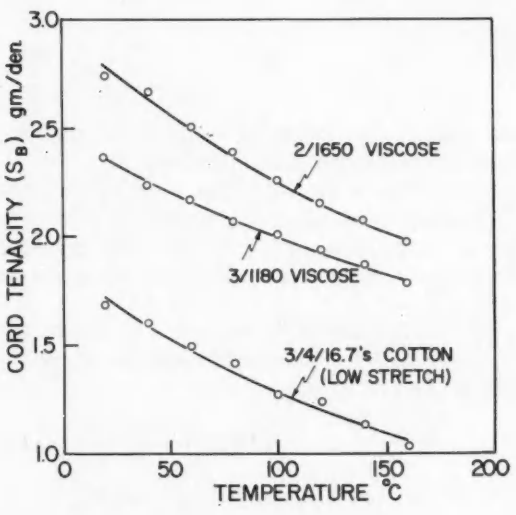

Fig. 11. Cord tenacity vs. temperature.

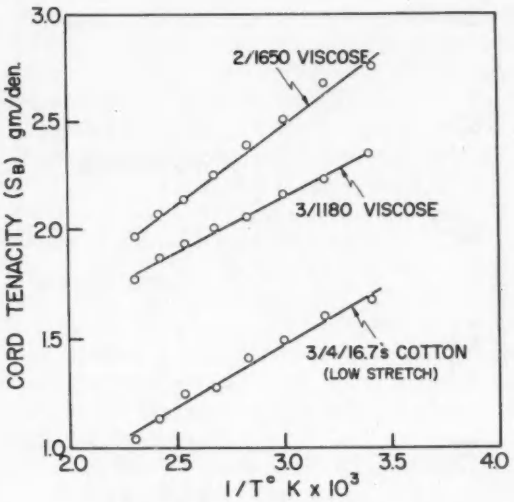

Fig. 12. Cord tenacity vs. reciprocal of absolute temperature.

useful. It is perhaps more important, from a practical standpoint, to evaluate the properties of the actual cords rather than the constituent yarns. It was also of interest to see how the yarn properties were modified by doubling into a cord.

The cords selected for study were a 2/1650 continuous-spun viscose cord, a 3/1180 pot-spun viscose cord, and a 3/4/16.7's steam-stretched cotton cord.

The experimental procedure was the same as that described in the previous section with the exception that the 30 individual Scott tests made at each temperature were done at the same time so that randomization was not as good as in the yarn tests. It was considered, however, that the procedure was adequate for the present investigation.

The variation of cord strength S_B expressed in grams per denier with temperature is shown in Figure 11, and in Figure 12, cord strength (S_B) is plotted against the reciprocal of the absolute temperature (T). As in the case of the yarns, it is clear that the breaking strength is, to a first approximation at least, a linear function of $1/T$.

The results of an analysis of variance are given in Tables V through VII.

TABLE V. 2/1650-Den. Viscose Cord

Source of variation	Analysis of variance: Sum of squares	Degrees of freedom	Mean square
Regression	258.18	1	258.18
Deviation from regression	2.10	6	0.35
Within temperatures (residual)	13.39	232	0.058

TABLE VI. 3/1180 Viscose (Pot-Spun) Cord

Source of variation	Analysis of variance: Sum of squares	Degrees of freedom	Mean square
Regression	140.57	1	146.57
Deviation from regression	0.36	6	0.60
Within temperatures (residual)	7.99	252	0.034

A comparison of the regression mean square with the residual mean square shows that the regression line is highly significant. The variance ratio for the deviation from regression is significant at the 1% level, thus indicating the possibility of some deviation from linearity. The major portion of the discrepancy was found to originate in the observations of 20°, 40°, and 80° C.

The best estimate of the regression coefficient was found to be 0.73×10^3 and the equation of the regression line,

$$S_B \text{ (g./den.)} = 0.298 + \frac{0.73 \times 10^3}{T} \qquad (5)$$

Here again the regression line is highly significant. The variance ratio for the deviation from regression is not significant at the 5% level. Thus in this case the deviation from linearity may possibly be neglected.

The best estimate of the regression coefficient was

TABLE VII. 3/4/16.7's Steam-Stretched Cotton Cord

Source of variation	Analysis of variance: Sum of squares	Degrees of freedom	Mean square
Regression	216.56	1	216.56
Deviation from regression	3.36	6	0.66
Within temperatures (residual)	12.30	232	0.053

found to be 0.502×10^3 and the equation of the regression line,

$$S_B \text{ (g./den.)} = 0.646 + \frac{0.502 \times 10^3}{T} \qquad (6)$$

As in the two previous instances, the regression line is highly significant. The variance ratio for the deviation from regression, 12.54, is highly significant at the 0.1% level, indicating deviation from linearity. The major portion of the discrepancy was found to originate in the observation at 20°, 120°, and 160° C.

The best estimate of the regression coefficient was found to be 0.58×10^3 and the equation of the regression line,

$$S_B \text{ (g./den.)} = -0.289 + \frac{0.58 \times 10^3}{T} \qquad (7)$$

The deviation from linearity in the case of the 2/1650 viscose cord and the cotton cord may possibly be attributed to (*a*) variation of cord quality and (*b*) the fact that in this series of experiments no provision was made for replication of the temperature. However, on examining the curves in Figure 12, it is evident that the deviation from linearity is not considerable, and the linear law is a good approximation. This is in agreement with the results obtained for yarns.

The effect of temperature on the strength of nylon and Terylene cords was investigated. Here certain complications arise because of the marked heat shrinkage of the synthetics, especially at temperatures beyond the region of 80° C. Preliminary experiments were carried out in which (*a*) the cords were preshrunk before testing and (*b*) the cords were clamped in the Scott jaws and heated to the required temperature while maintained at constant length. These experiments indicated that preshrinkage did not have any marked effect on the strength of the cords.

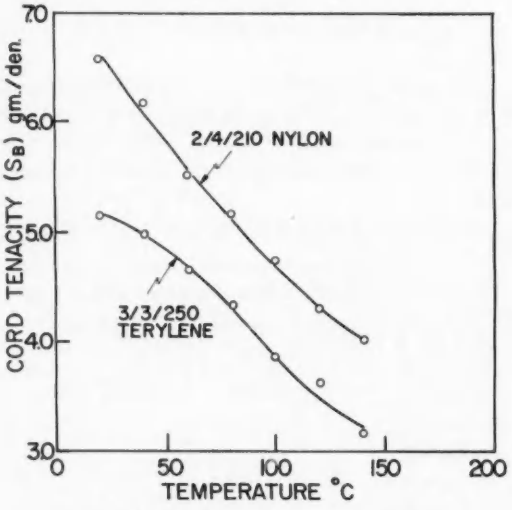

Fig. 13. Cord tenacity vs. temperature.

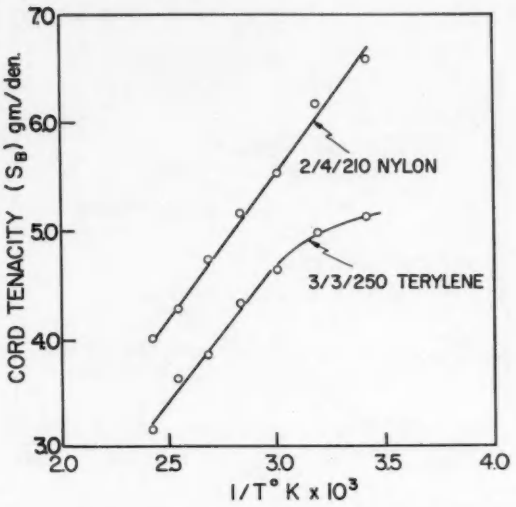

Fig. 14. Cord tenacity vs. reciprocal of absolute temperature.

In subsequent experiments to determine the variation of strength with temperature, the cords were allowed to shrink freely at the temperature at which the test was conducted. The variation of strength with temperature for the two cords tested, a 2/4/210 nylon cord and a 3/3/250 Terylene cord, is shown in Figure 13. In Figure 14, the breaking strength is plotted against $1/T$. It is clear from the latter curve that for nylon, the variation of strength with temperature follows the same pattern as previously found for rayon and cotton. In the case of Terylene, this appears to apply also at temperatures greater than about 80° C. Below 80° C., there appears to be marked deviation from linearity. It is perhaps significant that the second-order transition point in Terylene is in the neighborhood of 80° C. It is intended to carry out further work on these synthetic fibers with a view to checking these results.

In the tire industry the extension at a load of 10 lb. (E_{10}) is usually taken as a measure of the compliance of a cord, and the variation of this quantity with temperature gives some indication of the effect of temperature on tire growth.

The effect of temperature on the extension at 10 lb. for the rayon and cotton cords tested is shown in Figure 15. In all cases there is an exponential increase in the value of this quantity. It is evident that the E_{10} for cotton is much less influenced by temperature than that of either of the rayon cords. The E_{10} for the pot-spun viscose cord varies much more rapidly with temperature than does that for the continuous-spun viscose cord. The reduced extensibility of the latter yarn is probably responsible for this phenomenon.

The variation of the extensibility at break (E_{Br}) is shown in Figure 16. While the E_{Br} increases with temperature for the rayon cords, it decreases in the case of cotton. The behavior of cotton thus resembles that of Fortisan yarn.

In the case of nylon and Terylene, the measurement of extensibility at different temperatures presents some difficulty because of the heat shrinkage. Thus, at any given temperature, the extensibility will depend upon whether or not the material has been allowed to shrink. As far as tires are concerned, the cords are approximately held to length by the constraint of the surrounding rubber and the bead wire. In the variation of extensibility with temperature, the cord should not be allowed to shrink appreciably before testing.

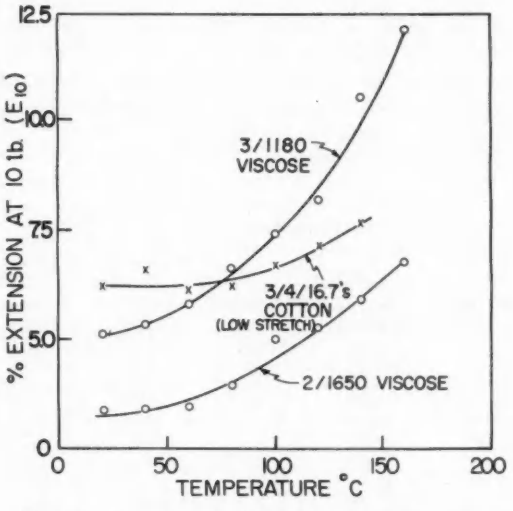

Fig. 15. Per cent extension at 10 lb. vs. temperature.

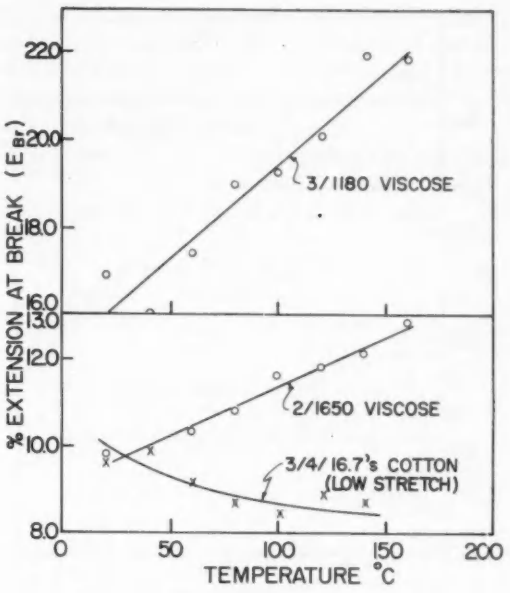

Fig. 16. Per cent extension at break vs. temperature.

As in Section 2.4, the product of the breaking strength, expressed in kilograms, and the extension at break (E_{Br}), is taken as a measure of the work to rupture. The values obtained for the two rayon cords are plotted against temperature in Figure 17. Although there is some scatter of the results, it does appear that the work to rupture is approximately independent of temperature. This was also found to be the case for viscose yarns. (See Section 2.3.)

2.5 Comparison of the Effect of Temperature on Yarn and Cord Strengths

It is of interest to compare the percentage change in yarn strength with the percentage change in the

TABLE VIII.

Temperature (° C.)	1650-den. continuous-spun viscose yarn	2/1650 cord	1180-den. pot-spun viscose yarn	3/1180 cord
20	0	0	0	0
100	20.0	18.1	17.0	14.7

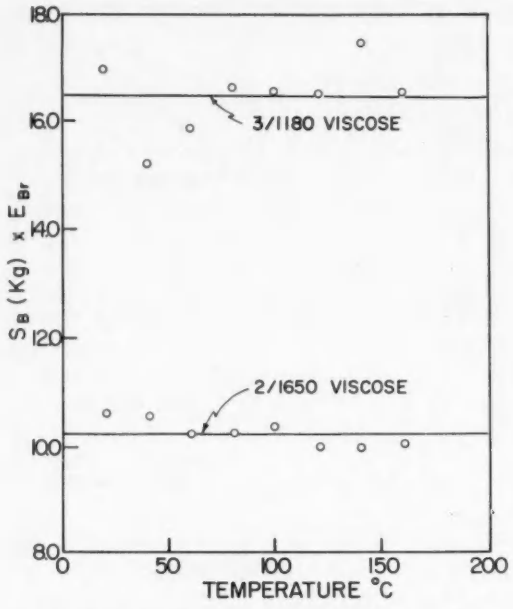

Fig. 17. Cord strength (kg.) × % extension at break vs. temperature.

strength of a corresponding cord for the same temperature change. Some comparative figures are given in Table VIII.

For both these yarns the percentage drop in strength is greater than for the corresponding cords. This is attributed to the increase in yarn extensibility at break with temperature, for this leads to an increase in the extension at break of the corresponding cords and a decrease in the twist at break. However, the change in twist compensates to some extent for the decrease in strength of the component yarns for a given increase in temperature.

The effect of yarn extensibility on cord strength may be calculated readily in the case of 2/1650, 12*s*/12*z* cord by means of the formula given below [10].

$$\frac{\text{Cord strength}}{2 \times \text{yarn strength}} = \left[1 - \frac{1}{108.3(1 + E_{Br})}\right] \times \sqrt{1 - \frac{1}{5(1 + E_{Br})^2}} \quad (8)$$

where E_{Br} is the percentage extension at break. The percentages of decrease in yarn strength at different temperatures with the calculated and experimental decreases in cord strength are listed in Table IX.

The agreement between calculated and experimental decrease in cord strength is reasonably satisfactory.

3. Theoretical Consideration

A number of attempts have been made to calculate theoretically the tensile strength of crystalline solids and inorganic glasses. In all cases the calculated values have been greatly in excess of the experimental values. In general these discrepancies have been attributed to the existence of surface cracks or to flaws in the crystal structure. Stress concentrations set up in the neighborhood of these flaws cause fractures which then spread through the solid. Considerations of this kind suggest that theoretical calculations of strength based on a molecular theory may have limited significance. Nevertheless such calculations may give an insight into the physical processes involved in fracture.

Mark [8], Meyer [9], and deBoer [2], have attempted to extend the theoretical treatment to calculate the tenacities of high polymers.

In the case of textile fibers, Mark [7] discusses two limiting cases. First, it is assumed that a break is due to rupture of the primary valence chains, second, that rupture of a fiber results from slippage of the chain molecules relative to one another.

The first hypothesis leads to a calculated tenacity of the order of 120 g./den. for cellulosic fibers. This value is approximately 13 times greater than the observed tenacities for well-orientated and highly crystallized natural and man-made fibers such as flex, hemp, ramie, cotton, Fortisan, etc.

TABLE IX. Comparison of Theoretical and Experimental Cord Strength

Temperature (° C.)	% Drop in strength of 1650-den. yarn	% Extension at break	% Drop in cord strength (2/1650, 12*s*/12*z*)	
			Experimental	Calculated
20	0	5.33	0	0
40	5.89	5.33	5.73	3.13
60	10.80	5.38	9.90	8.74
80	15.70	5.44	14.04	12.78
100	18.65	5.62	19.96	18.12
120	23.98	5.92	21.63	22.17
140	27.20	6.34	24.12	24.65
160	30.44	7.00	26.16	28.06

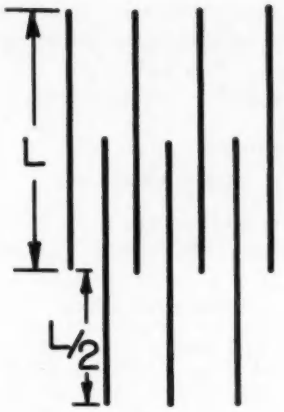

Fig. 18. System of regularly overlapping chains.

If it is assumed that well-orientated and highly crystallized fibers consist of regularly overlapping chains having a D.P. of about 400 as depicted in Figure 18, then the molecular slippage hypothesis leads to a calculated tenacity of about 10 g./den. for cellulosic fibers. This compares favorably with the value of 9 g./den. obtained, for example, in the case of Fortisan in a bone-dry state at 20° C.

Mark, in his calculation, does not take into account the thermal energy of the fiber. This thermal energy will assist the applied stress to cause rupture.

Kauzmann and Eyring [6] have shown that the mechanism of flow in high polymers is different from that in low molecular weight compounds. The unit of flow is no longer the entire molecule but a molecular segment which, in the case of the cellulosic molecule, may comprise several glucose residues. Under the action of an applied stress, the motion of polymer molecules may be regarded as a stress-biased diffusion process.

Application of Eyring's general theory of flow as rate process [4] to the model depicted in Figure 18 shows that the application of a stress will lead to a stress-biased diffusion of the molecules or molecular segments relative to one another. This process will continue until the molecules become completely separated, when rupture will occur. The rate at which two neighboring molecules move relatively to one another is given by

$$\frac{ds}{dt} = AT \exp\left(-\frac{\Delta F}{RF}\right) \sinh\left(\frac{Bf}{T}\right) \qquad (10a)$$

where A and B are constants, ΔF is the activation energy of flow, R is the gas constant, T is the absolute temperature, f is the applied stress, and s is the distance through which a molecule moves relative to the neighboring molecules.

If the stress is applied at a constant rate such that $f = Pt$, where t is the time, and P the rate of application of stress, then equation (10a) becomes

$$\frac{ds}{dt} = AT \exp\left(-\frac{\Delta F}{RT}\right) \sinh\left(\frac{BPt}{T}\right) \qquad (10b)$$

Rupture occurs when s becomes equal to $L/2$, where L is the chain length which is assumed uniform. When Pt is of the order of the breaking stress, $\sinh BPt/T$ may usually be approximated by $\frac{1}{2} \exp BPt/T$ so that equation (10b) becomes

$$\frac{ds}{dt} = \frac{AT}{2} \exp\left(-\frac{\Delta F}{RT}\right) \exp\left(\frac{BPt}{T}\right) \qquad (10c)$$

Integrating between the limits $S = 0$, $s = L/2$ and $t = 0$, $t = t_B$, and writing

$$f_B = Pt_B$$

where f_B is the breaking stress, we have

$$L = \frac{AT^2}{BP} \exp\left(-\frac{\Delta F}{RT}\right) \exp\left(\frac{Bf_B}{T}\right) \qquad (11)$$

Hence

$$f_B = \frac{\Delta F}{RB} - 2\frac{T}{B} \log\left(T \times \sqrt{\frac{A}{BPL}}\right) \qquad (12)$$

Since in the range of temperature 20° to 160° C., $\log T$ varies much more slowly than T, this is essentially a relationship of the form

$$f_B = \alpha - \beta T \qquad (13)$$

The above theoretical treatment is admittedly over-simplified. The chain molecules comprising a fiber are neither completely orientated nor completely crystallized. Irregularities occur in the molecular arrangement which may lead to localized stress concentrations. Tensions in certain chains may become relaxed by the process of slippage, with the result that the tensions in neighboring chains will be increased and possibly cause rupture so that this latter process cannot be ruled out. Further, the model employed does not include any mechanism for the delayed elastic recovery which occurs with textile fibers.

Both slippage and molecular rupture may be taken into account by a three-element model of the type used by Eyring [5]. Preliminary calculations in the case, however, again predict a linear relation between breaking strength and temperature.

It appears to the authors that experimental data over a wider range of temperature are needed before an adequate theory of strength can be developed.

4. Conclusion

It is concluded that the effect of temperature within the range 20°–160° C. on the bone-dry strength of cellulosic yarns and cords is to produce a change in strength which is related in a linear manner to the reciprocal of the absolute temperature. This also appears to be the case for nylon and Terylene, although in the latter instance this relationship may be modified by the existence of a second-order transition point. This conclusion is at variance with the result of a simple theoretical treatment which predicts a linear relationship to exist between the breaking strength and the temperature.

In all the yarns and cords investigated the extension at a given load increases with temperature. The extension at break may either increase or decrease with temperature. Thus an increase takes place for viscose rayon, whereas a decrease is observed for cotton. In the case of Fortisan, the extension at break is practically independent of temperature.

For the viscose rayon yarns and cords, the work to rupture is approximately independent of temperature. For cotton and Fortisan, on the other hand, an increase in temperature produces a decrease in this quantity.

Acknowledgment

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Influence of the Fiber Structure on the Nitration of Native Cellulose[1]

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Abstract

The nitration of native cotton cellulose has been investigated under both rate- and equilibrium-controlled conditions and in a manner that caused the least possible changes in the original fine structure of the fiber. By successive extractions the nitrates were subdivided into a number of fractions, which were examined for chemical composition and molecular weight, the fractionation being continued until swelling became noticeable.

The results indicated that the specimens studied were chemically nonuniform and more so the lower the average degree of substitution. Products formed in an equilibrium-controlled reaction or regenerated from solution were more homogeneous than similar ones obtained under rate-controlled conditions or with the original fiber structure left intact. The nitration involved an initial, rapid but only partial conversion of the surface and outer regions of the microfibrils of the cellulose, followed by a slower but more complete esterification of the interior, more crystalline portions, the easily accessible, short-chain parts being less substituted than the remainder of the material. In this respect nitrates were accordingly found to be different from most other cellulose derivatives.

THE role of the fiber structure is still the least understood of the factors influencing cellulose reactions. Recent investigations have shown that native cellulose is composed of microfibrils, 70 to 100 A in diameter and of considerable length. The surface and outer portions of these fibrils are supposed to be less highly organized than the interior and are always those parts of the fiber that are first converted in any cellulose reaction. Studies on the heterogeneous acetylation [8], methylation [21], and carboxymethylation [19] of cellulose have indicated that the initial stages of these reactions all involve a transition of the easily accessible portions of the fibrils to a high-substituted stage. The interior of the fibrils, on the other hand, reacts only slowly, although more rapidly the higher the degree of swelling of the reaction medium. Swelling is, as has long been known, a prerequisite for any conversion beyond the surface of the fiber, and when the ability to swell is impaired, for example by hornification of the microfibrils [18], reactivity is much decreased.

Nitration differs in many respects from other cellulose reactions. As carried out technically with a mixture of nitric acid, sulfuric acid, and water, this reaction is very rapid and involves a true chemical equilibrium. Hess and Trogus [7] considered nitration to proceed from the surface toward the interior of the micelles, but this concept soon met opposition as it was inconsistent with many of the known properties of cellulose nitrates. Miles and his co-workers [12 through 14] showed that although the intermicellar regions were undoubtedly first attacked, the nitric acid apparently was able to penetrate the whole fiber from the beginning. After the initial period, during which the nitrogen content reached a value of 7.5%, the nitrate groups were introduced randomly throughout the material with formation of trinitrate becoming prevalent after a nitrogen content of 12.8% had been attained. These results were later corroborated by Mathieu [11]. Chédin and Tribot [4, 5], in a series of investigations, concluded that only the planar nitric acid molecules are able to penetrate the cellulose crystallites, whereas the accessible localities are nitrated by a nitric acid–sulfuric acid mixture. Nitration is slower in baths of high viscosity, the rate of esterification apparently being a function of the rate of diffusion. Good solu-

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bility properties were considered to be effected more by uniform distribution than by the actual number of the nitrate groups introduced.

The aim of the present investigation was, first, to study the effect of the fiber structure on the nitration of a native cellulose and, second, to determine the degree of chemical nonuniformity of a series of cellulose nitrates. To avoid changes in the fine structure brought about by hydrolysis, a nitration mixture causing no degradation of the chain molecules was preferred to any of the technical mixtures. The nitrates were subdivided by successive extractions into a number of fractions, which were examined for chemical composition and molecular weight, but the fractionation was continued only until swelling began to affect the original fiber structure.

Results

The cotton linters used had an average degree of polymerization (D.P.) of approximately 1,700 and a Gaussian chain-length distribution [20]. Nitrations were all carried out with a mixture containing nitric acid, phosphoric acid, and phosphorus pentoxide, known to effect no degradation of cellulose. A total number of eight cellulose nitrates were prepared and fractionated. The nitrogen contents of these samples were determined by a semimicro Kjeldahl technique and their intrinsic viscosities were estimated in ethyl acetate and recalculated to be valid at a theoretical trisubstitution. Table I summarizes the results and shows that all specimens exhibited approximately the same intrinsic viscosity, *viz.*, 24–25 dl./g.

Sample 1 was prepared by diluting the standard nitrating mixture with phosphoric acid and samples 6–8 by using the original mixture under slightly varying conditions, the reaction time being enough to ensure equilibrium. Samples 2–5 were obtained under rate-controlled conditions. In this case nitration was carried out with the same nitration mixture at −32° C. for various lengths of time. The course of the reaction, as indicated by preliminary experiments, is seen in Figure 1, which shows an initial, rapid reaction, followed, after a nitrogen content of approximately 12% has been reached, by a much slower one.

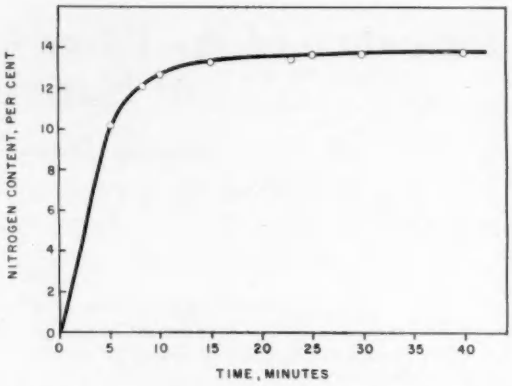

Fig. 1. Nitration of cotton linters at −32° C. with the standard nitration mixture.

For the fractional solution studies, mixtures of ethyl acetate and ethanol were used. The composition of the 14 different mixtures which could be applied before appreciable swelling occurred is given in Table II. Especially with lower substituted specimens, even the first mixtures were found to have too strong a solvent action, and in these cases a certain amount of water, different from sample to sample, had to be added to all of them. Duplicate experi-

TABLE I. Nitrogen Content and Intrinsic Viscosity of Samples No. 1 through 8

Sample No.	Nitrogen (%)	$[\eta]_T$
1	11.51	23.6
2	12.05	24.7
3	12.56	24.3
4	13.12	24.3
5	13.62	24.5
6	13.80	25.0
7	13.88	25.0
8	13.95	25.4

TABLE II. Composition of Solvent Mixtures Used for Fractional Extraction

Mixture No.	Parts ethyl acetate per 10 parts ethanol	Ethyl acetate (%)
I	9	47.3
II	10	50.0
III	11	52.4
IV	12	54.6
V	13	56.5
VI	14	58.3
VII	15	60.0
VIII	16	61.5
IX	17	62.9
X	18	64.3
XI	19	65.5
XII	20	66.7
XIII	21	67.7
XIV	22	68.7

TABLE III. Fractional Extraction of Sample No. 1 with Solvent Mixtures I, VIII, and XII, Containing 15% of Water

Fraction No.	Solvent mixture	Weight (%)	Nitrogen (%)
1	I	58.6	11.22
2	VIII	26.8	11.74
3	XII	7.7	11.92
4	Ethyl acetate	2.5	11.18
5	R_I*	4.4	11.08

* Residue insoluble in acetone.

TABLE IV. Fractional Extraction of Sample No. 2 with Solvent Mixtures I through XIV, Containing 10% of Water

Fraction No.	Weight (%)	Nitrogen (%)
1	11.3	12.04
2	1.3	11.87
3	2.5	12.16
4	1.1	12.19
5	1.3	12.15
6	1.1	12.00
7	1.1	11.88
8	0.7	12.05
9	1.1	12.23
10	1.2	12.45
11	1.3	12.40
12	1.0	12.55
13	1.0	12.25
14	0.9	12.22
R_S*	25.0	13.62
R_I	48.1	10.70

* Residue soluble in acetone.

TABLE V. Fractional Extraction of Sample No. 3 with Solvent Mixtures I through XIV, Containing 5% of Water

Fraction No.	Weight (%)	Nitrogen (%)
1	12.3	12.38
2	2.8	12.25
3	3.6	12.84
4	2.3	12.45
5	2.0	12.65
6	3.1	12.91
7	2.1	12.83
8	2.5	12.96
9	3.3	12.96
10	1.5	12.71
11	3.1	13.00
12	4.2	13.45
13	0.6	12.32
14	1.2	13.01
15*	9.8	13.47
R_S	1.5	12.82
R_I	44.1	11.66

* Extracted with undiluted mixture XIV.

ments indicated a good reproducibility, provided the extractions were carried out under identical conditions, and particularly at a constant temperature.

The first nitrate proved, as is seen in Table III, to be rather uniform chemically and could be subdivided into only five fractions, all of which exhibited about the same nitrogen content. Due to the limited solubility of the fractions in ethyl acetate, no intrinsic viscosities were determined, and the same applied to samples 2–4. Preliminary experiments showed that all fractions became soluble after renitration, but as the intrinsic viscosity was of a secondary importance in the present study, no attempts were made to apply renitration throughout these series. Tables IV through VII give the results obtained.

A total number of 14 and 15 fractions, respectively, could be isolated from samples 2 and 3 before appreciable swelling took place. The nitrogen contents showed considerable variations, which were reproducible, however, and therefore not caused by errors in nitrogen determinations, but probably by the fact that fractionation occurred according to both molecular weight and chemical composition. The

TABLE VI. Fractional Extraction of Sample No. 4 with Solvent Mixtures I through VII, Containing 2% of Water

Fraction No.	Weight (%)	Nitrogen (%)
1	12.6	12.70
2	6.3	13.15
3	6.5	13.14
4	6.3	13.12
5	3.2	13.08
6	7.8	13.16
7	6.0	13.23
R_S	22.0	13.59
R_I	29.3	12.55

TABLE VII. Fractional Extraction of Sample No. 5 with Solvent Mixtures I through IX

Fraction No.	Weight (%)	Nitrogen (%)	$[\eta]_T$
1	3.7	12.97	18.9
2	1.0	12.90	19.5
3	5.6	13.40	22.8
4	2.0	13.26	22.5
5	7.0	13.63	24.7
6	5.4	13.43	20.3
7	7.6	13.52	26.2
8	6.5	13.73	22.8
9	10.0	13.69	24.2
R_S	39.7	13.82	26.2
R_I	11.5	13.04	21.3*

* After renitration.

nitrate substitution was lowest for the first two fractions and increased slowly with proceeding fractionation. The remaining material could be divided into a portion soluble and insoluble, respectively, in acetone, the former of which exhibited a much higher and the latter a much lower average nitrogen content than the rest of the derivative. Samples 4 and 5 gave seven and nine fractions, respectively, with the same trends in variation of degree of substitution.

The intrinsic viscosities noted for sample 5 increased somewhat erratically from the earlier to the later fractions, but the range was only 7 dl./g. and did not reflect the true one, which extended from 8 up to 33 dl./g., as found in a previous study [20]. The average intrinsic viscosity of the fractionated material was approximately the same as the original, and this also applied to the remaining three samples, thus indicating the absence of any degradation. The corresponding nitrogen contents, however, were in many cases 0.2–0.3% lower than the original values, but it was uncertain whether the denitration occurred during fractionation or during drying.

The amount of material that could be extracted without swelling was approximately the same in all four cases as is seen from Table VIII, despite the fact that the nitrogen content of both the original and the extracted material varied. The degree of substitution accordingly seemed to be a factor of minor importance in this connection. Figure 2 indicates how complete solubility in acetone was achieved only after the nitrogen content of the insoluble portion had exceeded an approximate value of 13% (*cf.* 6). The frequency distribution of the substituents, given in Figure 3, shows clearly how the uniformity increased with increasing average degree of substitution.

Samples 6–8, which had been obtained under equilibrium-controlled conditions, were fractionally extracted in a similar way to yield 14, 12, and 12 fractions, respectively. The data in Tables IX–XI show the same general trend with degrees of substi-

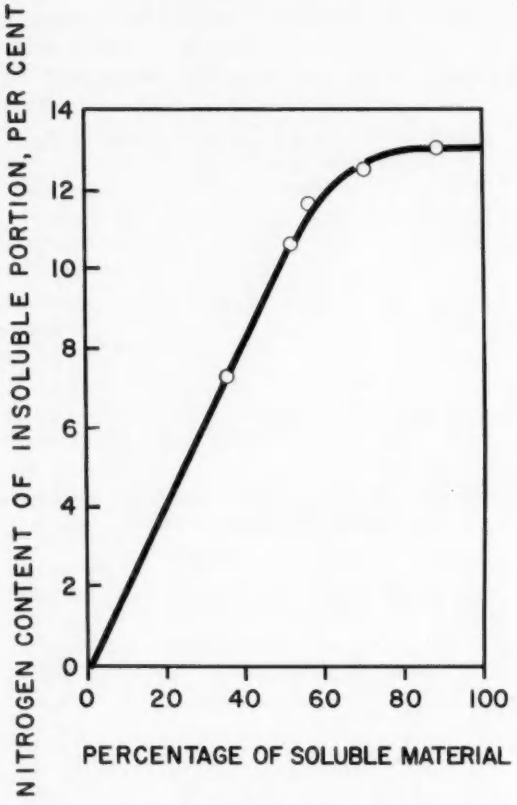

Fig. 2. Variation of nitrogen content with amount of material soluble in acetone.

TABLE VIII. Amount and Nitrogen Content of Material Extracted from Samples No. 2 through 5 Before Swelling

Sample No.	Average nitrogen content (%)	Amount extracted (%)	Nitrogen (%)
2	12.05	39.4	12.83
3	12.56	49.5	12.87
4	13.12	45.7	13.07
5	13.62	43.8	13.51

TABLE IX. Fractional Extraction of Sample No. 6 with Solvent Mixtures I through XIV, Containing 5% of Water

Fraction No.	Weight (%)	Nitrogen (%)	$[\eta]_T$
1	0.2	—	—
2	0.5	12.93	15.1
3	0.3	12.59	18.7
4	2.4	12.97	18.9
5	1.4	13.26	17.3
6	4.2	13.55	17.4
7	4.6	13.50	19.4
8	0.6	13.22	19.7
9	0.4	13.20	20.5
10	1.4	13.22	21.4
11	0.6	12.97	22.1
12	6.7	13.59	21.5
13	2.0	13.52	23.3
14	8.3	13.30	26.1
R_S	66.4	13.81	26.9

tution increasing with increasing intrinsic viscosities, the remaining, unfractionated portion exhibiting the highest nitrate substitution. These results are in agreement with data reported in several previous investigations [3, 15 through 17, 20, 22]. The integral and differential nitrate distribution curves reproduced in Figures 4–7 indicate the same uniformity for samples 6 and 7, whereas sample 8 evidently was much more homogeneous with only 15–20% of the material containing 12.8–13.7% nitrogen and the content of the remainder varying between 13.8 and 14.0%.

When the original fiber structure of sample 6 was destroyed by dissolving in acetone and reprecipitating in water, the product became more uniform chemically and, as is seen in Table XII, only nine fractions could be isolated. The average nitrogen content after precipitation was lowered to 13.51% and after fractionation to 13.36% and this removal of nitrate groups would render the results somewhat uncertain. The integral and differential curves in Figure 7 suggest a much higher chemical uniformity for the regenerated than for the native specimen, the frequency distribution of the former being very similar to that found for the highest substituted specimen.

TABLE X. Fractional Extraction of Sample No. 7

Fraction No.	Solvent mixture	Weight (%)	Nitrogen (%)	$[\eta]_T$
1	II	5.3	13.04	13.0
2	IV	4.3	13.27	16.4
3	V	3.0	13.37	19.8
4	VI	4.1	13.59	17.2
5	VII	3.4	13.47	20.7
6	VIII	3.3	13.32	20.1
7	IX	2.6	12.76	24.6
8	X	3.8	13.44	21.3
9	XI	4.6	13.60	22.7
10	XII	4.6	13.69	23.8
11	XIII	3.7	13.52	24.4
12	XIV	4.9	13.54	25.8
13	R_S	50.0	13.81	23.8
14	R_I	2.4	9.50	—

TABLE XI. Fractional Extraction of Sample No. 8

Fraction No.	Solvent mixture	Weight (%)	Nitrogen (%)	$[\eta]_T$
1	II	2.9	12.77	14.6
2	IV	1.8	12.98	19.7
3	V	1.6	12.80	23.5
4	VI	2.3	13.24	21.0
5	VII	9.1	13.60	22.1
6	VIII	1.6	13.31	20.9
7	IX	0.5	13.06	25.3
8	X	1.5	13.22	28.4
9	XI	4.1	13.78	23.1
10	XII	6.0	13.78	23.6
11	XIII	8.4	13.85	22.9
12	XIV	6.6	13.86	24.4
13	R_S	53.6	13.88	28.6

TABLE XII. Fractional Extraction of Regenerated Sample No. 6 with Solvent Mixtures VI through XIV, Containing 5% of Water

Fraction No.	Weight (%)	Nitrogen (%)	$[\eta]_T$
1	1.1	12.07	—
2	2.9	12.93	16.0
3	1.0	12.84	15.7
4	1.0	12.90	16.0
5	8.7	13.50	17.1
6	8.6	13.55	19.1
7	5.3	13.39	21.5
8	9.4	13.28	23.9
9	8.5	13.26	23.8
10*	53.5	13.40	31.4

* Extracted with undiluted mixture XIV.

Discussion

Fractional solution of a cellulose nitrate will, as it was performed here, be determined by three factors, namely, the fine structure of the fiber, the degree of substitution, and the degree of polymerization of the chain molecules. Of these, only the last two will be operative in the case of fractional precipitation, and this is the reason why this method is preferable, as was first shown by Jörgensen [9], when D.P. distributions are being studied. The solubility properties of cellulose derivatives are generally far more sensitive to changes in chemical composition than in molecular weight although, as was shown by Rosenthal and White [16] for cellulose acetates, the nature of the solvent-nonsolvent system used for frac-

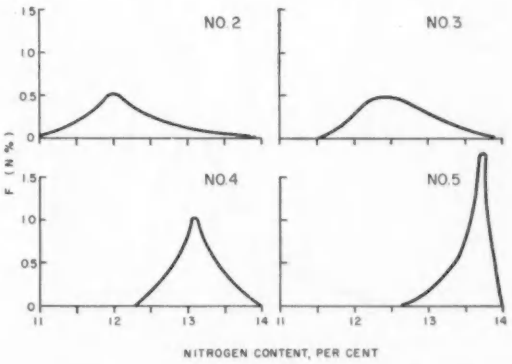

Fig. 3. Frequency distributions for samples 2–5.

tionation will also be of importance. In the case of fractional extraction with ethyl acetate–ethanol, the location of the molecules within the fiber and their chemical nature appear to be of as much importance as the length of the cellulose molecules.

The fractional solution probably first removed the shortest chains within the accessible regions, *i.e.*, those chains that were located on the surface of the microfibrils. At this stage, however, the extraction mixtures had a composition favoring solution of nitrates of an intermediate D.S., corresponding approximately to 12.5–13.5% nitrogen, and this effect was therefore probably superimposed on the other two. As extraction proceeded, material within the outer sections of the microfibrils was removed, first that of short chain-length and subsequently that of medium size. With the swelling beginning, the influence of the fiber structure will become less pronounced. If fractionation had been allowed to proceed beyond this stage, short- and medium-sized chains would have been extracted from the swollen gel, and when finally maximum swelling had occurred, chains of all sizes and substitutions would have been dissolved. Fractional solution is accordingly a very complicated process, and it is hardly surprising that earlier attempts to determine the polymolecularity of cellulose by this technique gave unsatisfactory results.

Elimination of the original native structure of the fiber would be expected to render the material more homogeneous from a morphological point of view. The results obtained showed that the regenerated cellulose nitrate was more uniform, both chemically and physically, than its native counterpart. The difference noticed between the two modifications was quite considerable, and this constituted an additional evidence of the great influence of the fiber structure on the course of fractional solutions.

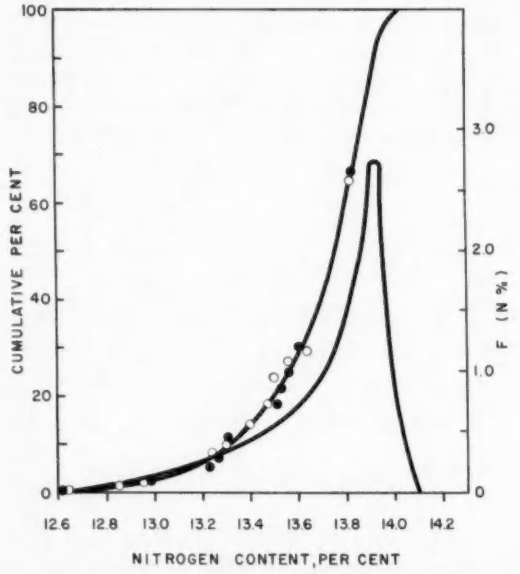

Fig. 4. Integral and differential distributions for sample 6.

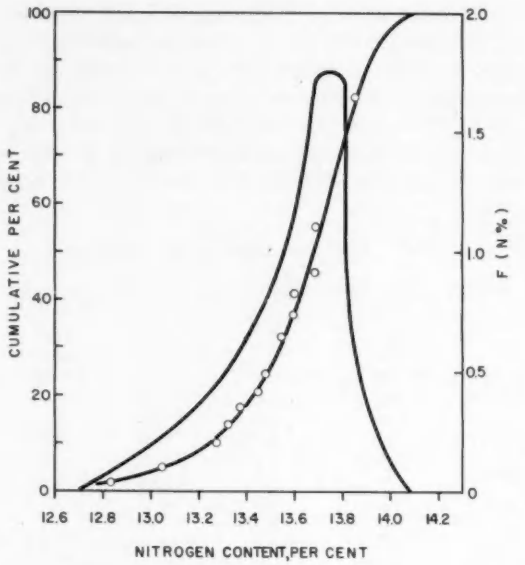

Fig. 5. Integral and differential distributions for sample 7.

The present results indicated that cellulose nitrates containing less than the maximum amount of nitrate groups and prepared from native cellulose are chemically nonuniform. This nonuniformity was more pronounced for products prepared in rate-controlled than in equilibrium-controlled reactions and decreased in both cases with increasing average degree of substitution. In this respect cellulose nitrates were accordingly similar to other cellulose derivatives, such as methyl- and carboxymethylcelluloses [19, 21], although the nonuniformity was evidently far more pronounced in the latter cases. The nitrate distributions contained only one maximum which was in agreement with previous results reported by Abadie [1] and by Smith [17] for cotton cellulose. The latter investigator, who applied a fractional-solution method similar to the present one, also studied a series of technical cellulose nitrates prepared from wood celluloses. In these cases the

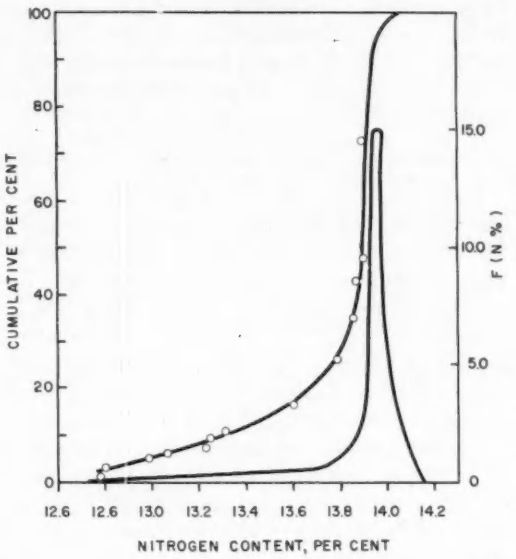

Fig. 6. Integral and differential distributions for sample 8.

frequency distribution was found to contain as many as three maxima.

Provided the above interpretation of the fractional extraction process is correct, the present data suggest that the nitrates investigated were more highly substituted in the interior of the microfibrils and along the longer chain molecules than on the surface or along the shorter chains. These conditions were exactly opposite to what is typical of other partially substituted cellulose derivatives. In these products, the accessible portions have, as was mentioned above, been found to contain far more, and the least accessible parts far less, substituents than the average, and in the case of acetylation and methylation, the surface of the microfibrils actually seems to become trisubstituted very rapidly.

The nitration apparently involved an initial, very rapid but only partial esterification of the surface of the fibrils, followed by a slower, but more complete, conversion of the interior, after which the accessible portions, gradually but only slowly, became more highly nitrated. If it be assumed according to Chédin [4, 5] that only the planar nitric acid molecules can enter the crystalline regions, this should, provided the water formed in the reaction could diffuse out, result in a higher degree of nitration in this region than in the accessible one, where phosphoric acid and phosphorus pentoxide would also be present. That the average degree of substitution is directly related to the ratio between the nitric and phosphoric acids present in the nitration mixture, has been definitely shown by Lindsley and Frank [10].

A similar distribution of nitrate groups was recently noted by Smith [17], who offered two possible explanations for the phenomenon, one involving stronger degradation and less esterification of the inner parts of the fiber due to dilution of the nitrating mixture, and another comprising denitration of the outer regions during isolation of the product. While the latter explanation seems improbable for several reasons, the former cannot apply in the present case, where a nondegrading medium was applied instead of the technical mixture used by Smith. A third, tentative suggestion by the same investigator therefore appears more likely, namely, that the longer chains in the original cellulose, mostly situated inside the fibrils, tended to become more highly nitrated than the medium or short ones.

Conclusions

The formation of the nitrate apparently takes place in a manner very different from that of most cellulose derivatives. Compared with other cellulose reactions, nitration is normally exceedingly rapid and involves, unlike many other esterifications, the establishment of a true chemical equilibrium. The

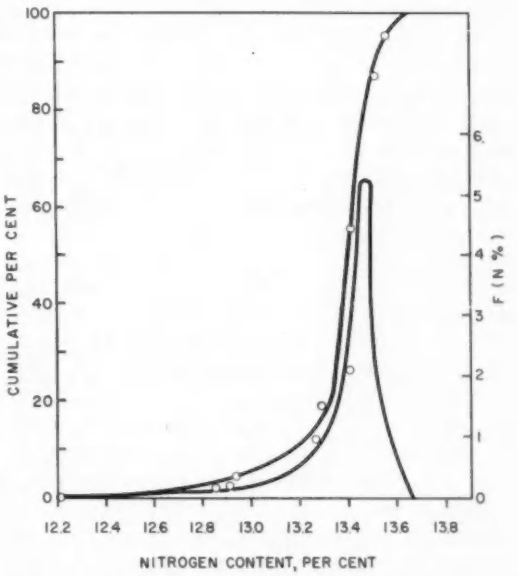

Fig. 7. Integral and differential distributions for regenerated sample 6.

products obtained are soluble in various solvents over a wide range of degree of substitution which is in sharp contrast to the acetates, for example, which have to be completely esterified to become fully soluble in organic solvents. These facts indicate a uniform distribution of the substituents in the nitrate derivative, probably brought about by the ability of the nitrating agent to penetrate the entire microfibril from the beginning of the reaction.

The results obtained here strongly support this interpretation but also indicate that this very ease of penetration of the nitric acid renders the final product somewhat nonuniform, the outer portions of the microfibrils being less converted than the interior, crystalline regions. This chemical nonuniformiity is undoubtedly of lesser magnitude than that of most other cellulose derivatives but is evidently still significant enough to influence the solubility characteristics of the product. Data from a recent fractional precipitation study [20] closely paralleled the present ones and showed the considerable influence of even a minor chemical nonuniformity on the molecular-weight distribution obtained.

Experimental

Materials

The cotton linters were an acetate-grade quality, kindly supplied by Drs. A. F. Martin and H. M. Spurlin, Hercules Powder Company, Wilmington, Del. Data for this material have been reported previously [20]. The nitration mixture was prepared according to the directions of Alexander and Mitchell [2]. Absolute ethanol and reagent-grade ethyl acetate were used in the extraction mixtures, and the latter solvent was also employed for the viscosity measurements, which were all carried out with a Cannon-Fenske viscometer.

Methods

Preparation of Samples 1–8. Sample 1 was prepared by nitrating cotton linters for 4 hr. at +5° C. with a mixture containing 50 parts by volume of the standard nitrating mixture and 50 parts of 85% phosphoric acid. Samples 2–5 were obtained by nitrating with the standard mixture for various lengths of time (10–30 min.) at a temperature of −32° C. The amount of material used varied between 5 and 10 g., and stirring was provided throughout the reaction. Lower temperatures were found to give a very viscous nitrating mixture which did not penetrate the fibers properly, whereas a higher temperature rendered the reaction too rapid to be followed. Samples 6–8, finally, were obtained under the same conditions as sample 1, although without any addition of phosphoric acid. All nitrates were recovered and purified as described elsewhere [20].

Fractionation

Cellulose nitrate, 5 g., was placed in a 500-ml. Erlenmeyer flask provided with a ground glass joint and a mercury-sealed stirrer. The extraction mixture, 450 ml., was added and fractionation allowed to proceed for 3 hr. with constant stirring in a bath maintained at 25 ± 0.02° C. The solution was removed by filtering through a sintered-glass filter funnel (Pyrex Coarse) and the residue washed thoroughly with fresh quantities of the same solvent mixture. In some experiments this extraction was repeated once, although very little additional material was removed. The solution obtained was evaporated nearly to dryness in a rotary evaporator, the remainder dissolved in acetone, and the extracted nitrate precipitated into water. Direct evaporation of the solvent mixture invariably left a residue containing 5–10% of solvent which could not be removed by drying. The white, fibrous precipitate was rinsed with distilled water and dried *in vacuo* for 2 hr. at 60° C.

The undissolved material was extracted in the same way with the next-following solvent mixture, and in this manner a maximum number of 14 fractions were obtained before swelling became noticeable. In most cases the unextracted portion was finally treated with acetone to yield one more fraction.

Analytical Procedures

Reduced viscosities were measured in ethyl acetate and after kinetic energy correction had been applied, extrapolated to zero concentration with Martin's equation. All values were recalculated to be valid at a theoretical trisubstitution by the relationship of Lindsley and Frank [10]. Nitrogen contents were determined by the semimicro Kjeldahl procedure referred to elsewhere [21].

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The authors wish to express their gratitude to Dr. C. B. Purves, E. B. Eddy Professor of Industrial and Cellulose Chemistry, McGill University, for his kind interest in the present investigation. Bernard Miller wishes to express his sincere thanks to the Celanese Corporation of America for two fellowships.

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The Effect of Partial Acetylation on the Pore-Size Distribution of Cotton Fabrics

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PARTIAL acetylation of cotton causes a considerable increase in the volume of the individual fibers since they increase in weight and decrease in density. For example, an acetylated cotton fiber containing 20% acetyl (dry basis) is theoretically 24.3% heavier than the original cotton and has a density of 1.450 g./cc. [5], as compared with a density of 1.550 g./cc. for the unacetylated. It follows that the volume of this acetylated fiber is 33% greater than that of the original cotton fiber and, assuming no change in length, the cross-sectional area is increased by the same percentage. Thus, the fiber may be said to have increased 33% in geometric coarseness.[3]

A yarn tends to increase in diameter during acetylation as its fibers increase in cross section. However, if lengthwise shrinkage is restrained, the resultant yarn would be under a much higher lateral compression. A yarn acetylated to 20% acetyl would have approximately the same gross geometric structure as a cotton yarn 33% heavier than the original unacetylated yarn and spun to the same number of turns per inch from a cotton of 33% greater geometric coarseness.

When a fabric is acetylated with minimum shrinkage, the yarn restraint is definitely present, and the individual pore spaces within the fabric boundaries would be expected to change in size as the fibers enlarge. This change should be reflected in the pore-size distribution of the void volume. To determine the nature and extent of these changes in the pore-size distribution in a fabric as the degree of acetylation is increased, measurements were made on a

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[3] The term "geometric coarseness" will be used rather than "geometric fineness" in order to avoid any ambiguity when referring to an increase in fiber volume or cross section.

graduated series of partially acetylated fabrics by means of the mercury-intrusion method. For comparison, measurements were also obtained for a fabric made from acetylated cotton fibers.

Method and Apparatus

The dilatometric mercury-intrusion method [7] is based on the application of external pressure to overcome the forces of surface tension which prevent the entrance of the nonwetting liquid mercury into the pores of an immersed sample [9]. The equation

$$pr = -2\sigma \cos \theta \qquad (1)$$

relates the applied pressure, p, to the effective radius, r, through the surface tension of mercury, σ, and its contact angle, θ, with respect to the material under test. As in the previous studies reported from this laboratory [2, 4, 8], 475 dynes/cm. and 140° were used, respectively, for the surface tension and the contact angle of mercury. These values, in conjunction with the proper conversion factors, reduce the equation to

$$pr = 105.6 \qquad (2)$$

where p is expressed in pounds per square inch absolute (p.s.i.a.) and r in microns.

Measurements are made of the cumulative volume of mercury forced into the pores of the immersed sample at each successive pressure, as the pressure on the system is increased by increments. From these data, the distribution function, $D(r)$, can be calculated to show the distribution of void volume by pore sizes.

The sample chamber of a commercially available porometer [6] was modified to hold a fabric sample in the form of a disk in a horizontal plane. The new chamber, with a maximum inside diameter of 2 7/8 in., is very shallow at the periphery and increases to a depth of 13/16 in. at the center line, i.e., the distance between the channel entries. The differential pressure between the upper and lower boundaries of the sample is small, a matter of importance when considering the pores of larger radii. In the deep and narrow standard chamber, the pressure differential corresponds to a wide spread in pore sizes at low pressures and does not become negligible until approximately 10 p.s.i.a. (10 μ effective radius). With the modified sample chamber, the range is very small at the beginning of an experiment and becomes negligible rapidly as the pressure is increased. Thus, the sizes of the pores which are filled at the beginning

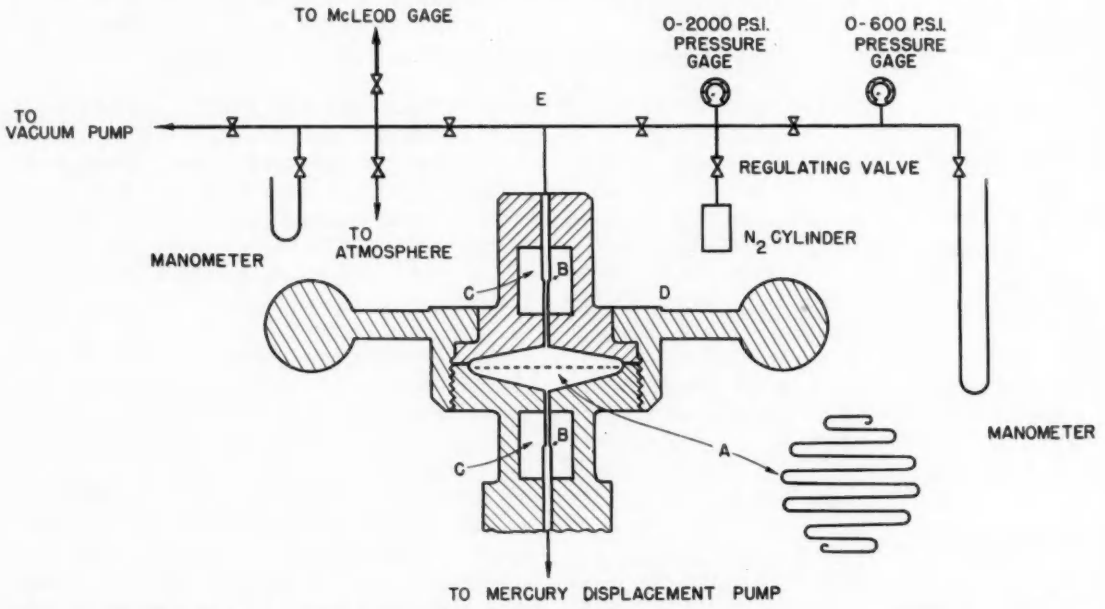

Fig. 1. Schematic drawing of modified sample holder and auxiliary equipment. A, top view of wire support and its position in sample chamber; B, reference divisions in channels; C, lucite windows; D, compression nut; E, manifold.

of an experiment in the new sample chamber more nearly approximate those corresponding to the pressures recorded.

For fabrics, three apparatuses of overlapping pressure ranges were used previously [4] to obtain the pore-size distribution curves over an extended pore-size range. This necessitated the calibration of three dilatometers and the use of three different specimens. In addition, the details of the experimental procedures for the three dilatometers were slightly different. Using the modified sample chamber on the commercial porometer, the data for a range of pressure from 0.81 to 1000 p.s.i.a. (130 to 0.1 μ effective radius) can be obtained on one specimen in one unbroken run and in less than one third the time needed to make the split runs.

Procedure

Circles, 2.5 in. in diameter, were cut from the samples. Their thicknesses were measured by A.S.T.M. Procedure D39-39, and their dry weights were determined. A stainless-steel wire, bent back and forth in a plane (Figure 1, A), was placed between the two disks of a specimen to achieve some degree of separation of the disks. An identical wire support was placed over the top disk in the chamber in order to hold the specimen in a fixed horizontal position and to prevent it from floating to the top of the chamber. When a single disk was used, it was placed between the wire supports.

The experimental procedure was essentially the same as that previously described [8]. In brief, the volume of the chamber was determined, and the pressure-volume correction curve was established with only mercury and the stainless-steel wire supports in the chamber. With the specimen in place, the system was thoroughly evacuated. The porometer scales were set to read uncorrected bulk volume directly, and the diminution in volume was followed over a pressure range from 0.81 to 415 p.s.i.a. This maximum pressure was considered adequate for textile materials, because the filling of the void volume was approximately completed and the volume changes at higher pressures were of the same order of magnitude as the accuracy of a reading.

A modification of the previous method of calculating the distribution curves was used. By means of Equation 2, the corresponding radii were calculated directly from the experimental pressure values and were plotted against the corrected bulk volumes (Figure 2, A). The slope of this curve, dV/dr, is the distribution function, $D(r)$, which may be defined as the rate at which the void volume changes as the pore radius increases, since the change in bulk volume is identical to the change in void volume. The point of inflection in the radius-volume curve, therefore, marks the position of the maximum (or peak) in the distribution curve and can be located by inspection.

The distribution curve (Figure 2, B) was established by plotting the slopes obtained graphically at selected radii. The values for the distribution function thus determined are in terms of cc./μ per specimen and may be converted to any units desired, such as cc./μ/g. of sample or cc./μ/cc. of sample, by the application of the appropriate factor. Regardless of which units are used, the peak of the distribution curve remains at the same pore-radius position, but the relative positions of the entire curves for different samples may vary depending upon the units selected.

Samples

Commercial cotton sheeting (48 × 44) was desized and scoured. It had a conditioned weight of 4.5 oz./sq. yd. Portions were partially acetylated [1, 3] to obtain seven different lots having acetyl contents ranging from 4.7% to 28.2% (dry basis). These eight fabrics formed the fundamental basis for this study. For comparative purposes, a pair of 2/1 twills were included which had been constructed, respectively, from Iquitos cotton and from Iquitos

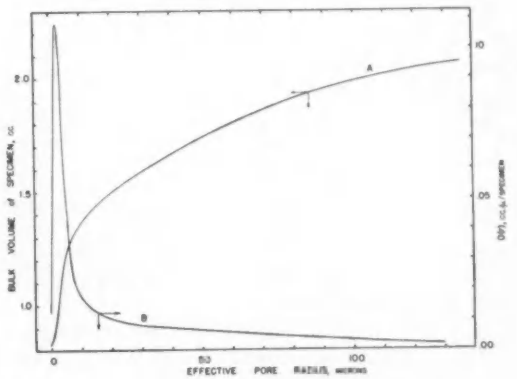

Fig. 2. Typical manner of plotting data. A, bulk volume at radii which correspond to pressure applied; B, complete pore-size distribution curve.

fibers after partial acetylation in the fiber form to 17.4% acetyl (dry basis). The latter two fabrics were alike in respect to yarn numbers, turns per inch in the yarns, thread count, and dry weight (9 oz./sq. yd.). Peruvian Iquitos is very coarse cotton. In this instance it had a weight fineness of 8 μg./in.

Some calculated and experimentally determined properties of the 10 samples are listed in Table I.

Results and Discussion

Cotton Sheeting Series

The results for the cotton sheeting series are expressed in terms of cc./g. of unacetylated fabric or that weight of sample which is equivalent to 1 g. of the unacetylated. Thus, the data show the changes which occurred in 1 g. of the original sheeting as a result of acetylation to various percentages, ranging from 4.7 to 28.2%.

An over-all picture of the experimental data (Table II) is shown by the bar graphs in Figure 3. The solid areas represent the volumes of the fibers as calculated from fiber densities and acetyl percentages, while the dotted lines, immediately above these sections, correspond to the bulk volumes read at the final pressure of 415 p.s.i.a. (0.25 μ). The upper limit of each bar is based on values obtained at the initial experimental pressure, i.e., 0.81 p.s.i.a. or 130 μ effective radius. The measured void

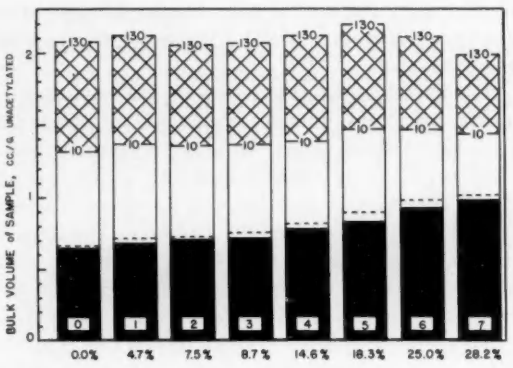

Fig. 3. Sheeting series. Experimental bulk volumes per gram of unacetylated at 130, 10, and 0.25 μ effective radii and theoretical bulk volumes of fibers. The figures below the bars are per cent acetylation. Cross-hatch, interyarn void volume. Open, interfiber (intrayarn) void volume. Solid, fiber volume.

volumes are separated into interyarn and interfiber regions at 10 μ (10.56 p.s.i.a.).

Fiber Volumes. There is a regular increase in the calculated fiber volume as the acetyl content is increased. If the increase in fiber coarseness is plotted against the degree of acetyl substitution, the relationship is practically linear. The bulk volumes measured at 415 p.s.i.a. (0.25 μ) tend to parallel the calculated values but are slightly larger consistently. This is to be expected since the pores with radii less than 0.25 μ would not have been

TABLE I. Some Experimentally Determined and Calculated Properties of the Samples

	Fibers				Fabrics	
Sample	Acetyl (%)*	Weight increase (%)†	Density (g./cc.)‡	Coarseness increase (%)§	Thread count (warp×filling) per inch	Thickness (cm.)
Cotton sheeting series						
0	0.00	0.0	1.550	0.0	48.6×47.4	0.0338
1	4.65	4.8	1.534	5.9	50.4×46.0	0.0333
2	7.48	7.9	1.526	9.6	49.6×46.8	0.0330
3	8.69	9.3	1.518	11.6	49.4×46.6	0.0333
4	14.57	16.6	1.486	21.6	49.0×46.4	0.0330
5	18.28	21.7	1.466	28.7	51.0×46.8	0.0351
6	25.04	32.4	1.425	44.0	50.6×47.4	0.0371
7	28.17	38.0	1.408	51.9	49.2×50.8	0.0386
Twill pair of Iquitos cotton						
A	0.00	0.0	1.554	0.0	59.0×41.0	0.0575
B	17.43	20.5	1.464	27.9	58.2×40.2	0.0637

* All acetyl percentages on dry weight basis.
† Theoretical increase calculated from acetyl content.
‡ By flotation method [5].
§ Calculated from weight increase and density ratio.

TABLE II. Averaged Experimental Data

	Sheeting series								Iquitos	
Sample designation	0	1	2	3	4	5	6	7	A	B
Acetyl, %	0.0	4.7	7.5	8.7	14.6	18.3	25.0	28.2	0.0	17.4
Pore-radius position of $D(r)$ peak, μ	4.2	3.8	3.5	3.2	2.7	2.8	3.0	2.8	5.5	5.2
Yarn porosity, %*	50.6	50.0	47.9	47.1	43.3	43.5	36.6	31.8	42.9	37.3
	cc./g. unacetylated sample								cc./g. sample	
Bulk volume, cc., at										
130 μ	2.082	2.128	2.062	2.072	2.124	2.200	2.114	1.989	1.759	1.713
10 μ	1.306	1.367	1.358	1.362	1.385	1.470	1.466	1.437	1.128	1.090
0.25 μ	0.667	0.714	0.730	0.759	0.815	0.893	0.976	1.021	0.654	0.699
of fibers†	0.645	0.683	0.707	0.720	0.785	0.830	0.929	0.980	0.644	0.683
Void available, cc., at										
130 μ	1.437	1.445	1.355	1.352	1.339	1.370	1.185	1.009	1.115	1.030
10 μ	0.661	0.684	0.651	0.642	0.600	0.640	0.537	0.457	0.484	0.407
0.25 μ	0.022	0.031	0.023	0.039	0.030	0.063	0.047	0.041	0.010	0.016
Void, cc., between										
130–10 μ	0.776	0.761	0.704	0.710	0.739	0.730	0.648	0.552	0.631	0.623
10–0.25 μ	0.639	0.653	0.628	0.603	0.570	0.577	0.490	0.416	0.474	0.391

* Calculated: (Void available at 10 μ divided by bulk volume at 10 μ) × 100.
† Theoretical calculated values.

filled, and the bulk volumes measured by the porometer at the final experimental pressure would be larger than those calculated from fiber densities and acetyl percentages.

Interfiber Void Volumes. The upper limit of pore sizes in the interfiber region has been set at 10 μ effective radius, which is considered to mark approximately the initial entry of mercury into the interfiber or intrayarn voids as the pressure is increased. The choice is based on the fact that, as the pore radius decreased, the slope of the radius-volume curve (Figure 2, A) increased more rapidly in the vicinity of 10 μ effective radius, or the distribution curve (Figure 2, B) began a sharp upward sweep to a peak, either of which may logically be interpreted to mark the comparatively sudden availability of spaces whose pore entrances were about 10 μ. Furthermore, it has previously been shown [2] that the peak region in the distribution curve is predominantly a measure of interfiber pore sizes. However, 10 μ is not intended as a sharp separation between interfiber (intrayarn) and interyarn regions since there probably was a gradual transition from one to the other, nor is it intended as an inflexible boundary for all samples since the enlargement of the fibers modified the sizes of all the interfiber voids, including those at the upper limit of this range.

In Figure 3, the only marked differences in total interfiber volumes occur in the more highly acetylated fabrics where the diminution in volume is evident. However, a downward trend throughout is more apparent in Figure 4, when the per cent acetyl is plotted against these volumes.

A further and more effective analysis of the interfiber void volumes is accomplished by means of the distribution curves (Figure 5) which apportion the total interfiber void volumes according to pore sizes so that the area under any part of a curve equals the

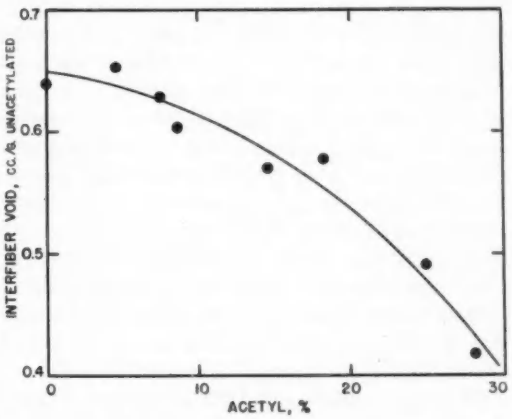

Fig. 4. Sheeting series. Interfiber void volume, on the basis of a gram of unacetylated, *vs.* per cent acetyl.

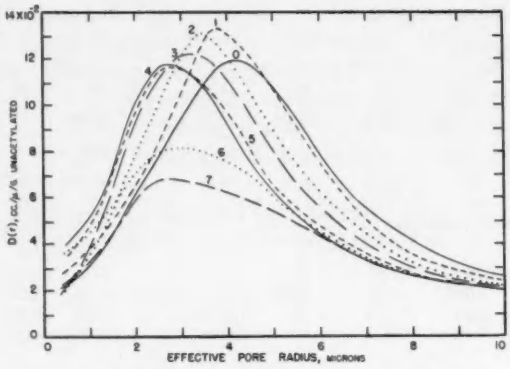

Fig. 5. Sheeting series. Pore-size distribution curves in interfiber regions.

total volume of the pores having radii between the selected limits. As the per cent acetyl increased, the peak of the distribution curve, corresponding to the predominant interfiber pore radius, shifted downward from the 4.2 μ pore-radius position for the unacetylated (curve 0) to the 2.8 μ pore-radius position for the fabric containing 14.6% acetyl (curve 4) and was little affected by further acetylation up to 28.2% acetyl. The peak shift is probably dependent upon a compromise between the opposing influences of fiber size and of degree of packing. The coarser and rounder the fiber, the higher is the pore-radius position of the peak for the same degree of packing [8] and the more tightly packed a given fiber sample, the lower is the pore-radius position of the peak [4]. When fabrics are acetylated, both factors are involved. As the degree of acetylation was increased, the fibers increased in coarseness and with the exception of sample 5, the packing became progressively tighter. The degree of packing is converse to what might be called yarn porosity, which is equivalent to the void volume within the yarn expressed as percentage of the bulk volume of the yarn (volume at 10 μ). On this basis, the yarn porosity decreased as acetylation was increased up to 14.6% (sample 4), remained unchanged for 18.3% acetyl (sample 5), then decreased more markedly.

The packing effect dominated through sample 4 as reflected in the initial downward progression of the pore-radius position of the distribution-curve peaks. Since the shift was accomplished by a displacement of the entire interfiber distribution curve toward a lower pore-radius position, each void space must have been diminished in size by the enlargement of the fibers.

Sample 5 (18.3% acetyl) marked the transition to a different type of change. The porosity (43.5%) of this yarn, and therefore its degree of packing, was the same as that of sample 4 (14.6% acetyl). As a result, the relative coarseness of the fibers should determine the locations of their peaks with respect to each other. As can be seen in Figure 5, not only the peak but also the whole interfiber distribution curve for sample 5 actually lies at a slightly greater pore-radius position than that of sample 4.

In the two most highly acetylated samples, the continued enlargement of the fibers against the yarn-twist restraint resulted in distorted fiber cross sections since the space available within the yarn was limited. In contrast to the comparatively uncrowded fibers of the unacetylated (Figure 6, I), the adjacent fibers of the 28.2% acetylated sample (Figure 6, II) were pressed against each other extensively and the interfiber spaces were flattened and smaller. The more nearly slotlike the configuration of a pore, the closer its *effective* radius approximates the distance between the sides of the pores. This can be shown mathematically by a consideration of the relationship upon which Equation 1 is based. Therefore, it is not difficult to imagine pores of progressively narrower and more slotlike configuration having the same effective radius.

Interyarn Void Volumes. The discussion of void volumes within this range is best based on results obtained when single disks were used, since significant differences had been noted between the 2-disk and the 1-disk specimens in the higher pore-radius range in the fabrics of lower acetyl content and in the unacetylated. This difference could conceivably be attributed to the space between the two disks.

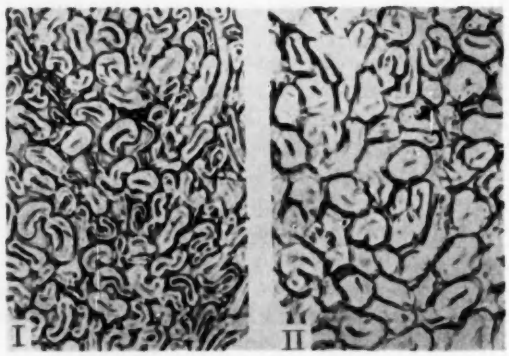

Fig. 6. Cross section of fibers in yarns (500×). I, sample 0; II, sample 7.

The only consistent trend was the decrease in total interyarn void volume for the samples containing more than 18.3% acetyl (Figure 3). The same progression was maintained for the three samples throughout the greater portion of the pore sizes covered by this radius range, as shown by the distribution curves in Figure 7. These three samples were the only ones in which any significant variation in distribution of void volumes within the interyarn region was observed.

A shallow peak appeared frequently on the interyarn distribution curve in the vicinity of 60 μ; however, its appearance was consistent neither in position, height, nor duplicability except for sample 5 in which a shallow peak was evident at 55 μ for all specimens (2 disks or 1 disk). Two explanations are suggested: (1) the peak is real and characterizes a particular portion of the interyarn void volume, which portion may vary from specimen to specimen due to some nonuniformity of the fabric, or (2) the peak is accidental in that it might be associated with the manner in which the wire supports were pressed against the specimen.

Total Void Volumes. The total void volume (130 to 0.25 μ) showed a general downward trend as acetyl content increased (Table II). Here again, the only markedly definite decrease occurred in the most highly acetylated samples. Up to an acetyl content of 18.3% (sample 5), the void volumes within each of the three ranges (total, interyarn, and interfiber) decreased by less than 11% of the corresponding volumes in the unacetylated sample. For the 25 and 28.2% samples, the reductions in volume were about 20 and 30%, respectively.

Surface Void Volumes. The upper limits of the bar graphs in Figure 3 are the bulk volumes of the samples as measured on single-disk specimens at 0.81 p.s.i.a. (130 μ effective radius). This experimental starting pressure was equal to the head of mercury above the sample and had little significance of itself but refers, in a general way, to the surface irregularities of the fabrics. Two factors which might affect the measured volumes at 130 μ are (1) the compression of the fabric as a whole and (2) the filling of the surface depressions. Obviously, the more compressible a fabric, the smaller will be its bulk volume at 130 μ. Likewise, the more sharply defined the surface depressions, the more readily will the mercury penetrate therein.

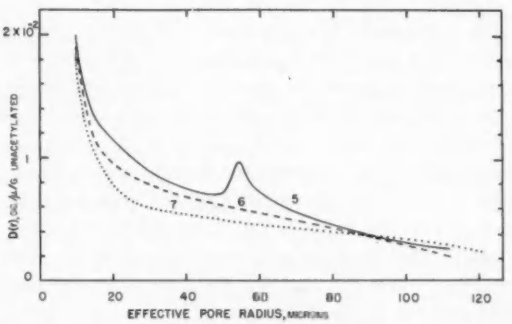

Fig. 7. Pore-size distribution curves for samples 5 through 7 in interyarn region.

As the fibers were enlarged by acetylation, the fabrics decreased in softness and in susceptibility to compression. This might explain the upward trend in bulk volume at 130 μ from the unacetylated through sample 5. This latter sample may be considered to mark the shift in dominance from the factor of compression to that of filling the surface depressions.

The fibers of 18.3% acetyl (sample 5) had been enlarged to such an extent that the cross section of the yarn was markedly increased (corroborated by increased fabric thickness). Since the expansion was constrained by the tightness of the yarn twist, this yarn may be considered to be relatively hard. Further coarsening of the fibers produced even harder yarns. From samples 5 through 7, the hardened yarns were more definitely delineated as entities. The increased tightening of the yarn increased this delineation, which, in turn, more sharply accentuated the surface depressions, thus making them more accessible to the entry of mercury. This might explain the pronounced decrease in bulk volume at 130 μ from samples 5 through 7, as shown in Figure 3 and Table II.

It must be emphasized that the relationships between void volumes are strictly applicable only to this particular series of fabrics. For instance, some variations in data, such as shown in Figure 4, may be caused by inadvertent differences in the mechanical manipulation at some step in the acetylation procedure, differences which have no correlation with acetyl content *per se*. For another group of fabrics, the relationships may differ since the over-all void-volume distribution is influenced by such variables as fiber coarseness, yarn construction (in particular, yarn porosity), closeness and type of weave in the unacetylated fabric, and/or whether the cotton is acetylated in the fabric, yarn, or fiber form. A pair of fabrics which differ from the sheeting series in all the variables mentioned is discussed in the following section.

Similar Fabrics from Unacetylated and Acetylated Iquitos Fibers

In the cotton sheeting series the fibers increased in coarseness and weight as they were acetylated *in situ* within the fabric structure so that the linear density of the yarn increased. The yarns of sample B were spun from Iquitos fibers after acetylation to 17.4% and were of the same linear density as those of sample A, the unacetylated member of the pair. Consequently, for every 100 fibers in the cross section of the unacetylated, there should have been only 83 fibers in that of the acetylated yarn, since each fiber theoretically had increased 20.5% in weight. The fabrics woven from these two yarns were as nearly alike in construction as possible.

The data have been calculated as per gram of sample in order to keep the acetylated fabric on a comparable basis with its unacetylated companion (Table II and Figure 8).

Fiber Volumes. Though the yarns in samples A and B had the same linear density, they did not have the same volume of fibers per unit length, since the weight increase of 20.5% corresponded to a volume increase of 27.9% (Table I). Thus, the volume of fibers per unit length of yarn (or per gram of fabric) was actually about 6% greater for sample B than for sample A. The bulk volumes measured at 415 p.s.i.a. (0.25 micron effective radius), represented by the broken lines in Fig. 8, I, closely approximated the calculated fiber volumes represented by the solid areas.

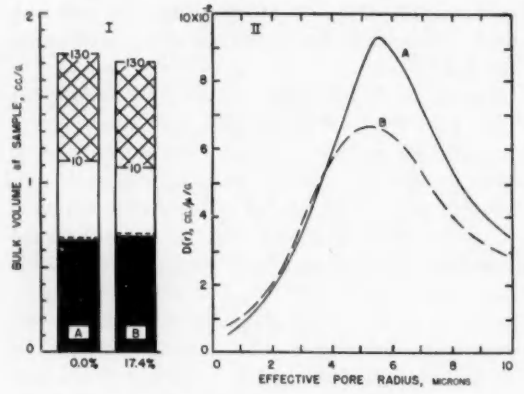

Fig. 8. Twill fabrics, Iquitos cotton. I. Experimental bulk volumes per gram of sample at 130, 10, and 0.25 μ effective radii and theoretical bulk volumes of fibers. The figures below the bars are per cent acetylation. Crosshatch, interyarn void volume. Open, interfiber (intrayarn) void volume. Solid, fiber volume. II. Pore-size distribution curves in interfiber region.

Interfiber Void Volumes. The experimental void volume per gram within the interfiber region for sample B was 17.5% less than that for sample A, as shown by a comparison of the appropriate sections of Figure 8, I, or of the areas beneath the curves in Figure 8, II. Taking 10 μ as the upper limit of the pore sizes within the yarns, the bulk volumes at 10 μ (1.128 cc. for sample A and 1.090 cc. for sample B) can be considered equal to the bulk volumes of the yarns per gram. Thus, the fibers of sample B must have been compressed into a 3.5% smaller volume than those of sample A. This is not illogical since more pressure would be necessary to put the same number of turns per inch into a yarn containing a 6% larger volume of fibers. This fiber-volume relationship between samples A and B was essentially the same as that between samples 0 and 1 of the sheeting series.

There were two important differences however. In the first place, the yarns of the sheeting pair had the same number of fibers per cross section, each individual acetylated fiber having, theoretically, a 6% greater geometric coarseness than the unacetylated, while the yarn of the unacetylated sample A had 100 fibers per cross section to every 83 fibers in the yarn of the acetylated sample B, each fiber of the latter having a 27.9% greater geometric coarseness than the unacetylated Iquitos. Second, the yarn porosity of sample 0 (50.6%) was considerably greater than that of sample A (42.9%); therefore, it follows mathematically that the reduction of both void volumes by the same absolute value (6% of a given volume of unacetylated cotton) would be expected to have a relatively smaller effect on the yarn porosity progressing from samples 0 to 1 than from samples A to B. This is qualitatively consistent with the relative yarn porosities shown by these pairs (Table II).

As explained in the discussion of the sheeting series, increased fiber coarseness and tighter packing would tend to shift the peak position of the distribution curve in opposite directions along the radius axis. In each of these pairs, the peak position of the acetylated fabric was 1/2 μ lower in pore-radius position than its unacetylated counterpart. Therefore, it can be concluded that the differences in degree of packing in each pair outweighed the differences in fiber coarseness to approximately the same extent. Unlike the sheeting pair, in which the peak shift was due to the displacement of the whole interfiber distribution curve toward a lower pore-radius position, the shift in the twill pair resulted from the

concentration of the void-volume loss within the 4–10 μ range.

Interyarn Void Volumes. The interyarn void volumes of both fabrics were approximately equal and, in fact, the distribution curves practically coincided at pore radii above 15 μ. This would be expected since the fabrics were woven as nearly alike as possible. Therefore, there was no paralleling of void-volume losses in the interyarn and interfiber regions with acetylation; the loss in interyarn void was only 1.5% as compared with a loss in interfiber void of 17.5%.

Summary

Partial acetylation increases the weight and decreases the density of a cotton fiber, and as acetylation increases, the coarseness of the fiber increases rapidly. When acetylation is carried out on either yarns or fabrics, the geometric structure of the sample changes so that the yarns become tighter and the fabrics denser according to the restriction placed on the enlarged fibers. In order to gain some insight into the structural modification of a fabric after partial acetylation, the pore-size distributions of the void volumes within the fabric boundaries were determined on a cotton-sheeting series, whose acetyl content ranged from 0.0 to 28.2% acetyl.

A modified sample holder for a porometer has been developed which permits the measurement of the bulk-volume changes in a fabric over the whole pressure range from 0.81 p.s.i.a. (130 μ, effective radius) to the limiting pressure of the instrument in one continuous run on a single specimen. A maximum pressure of 415 p.s.i.a. (0.25 μ) has been found adequate for the fabrics included in this study.

The distribution function has been determined from experimental data by a method somewhat different from that customarily used. The general characteristics of the distribution curve can be judged by inspection from the manner in which the bulk volume changes with effective radius, the latter being calculated directly from the applied pressures.

As the acetyl content of the sheeting samples increased, there was a general downward trend in total void volume within the interfiber region. Further analysis of the interfiber (intrayarn) void volumes by means of pore-size distribution curves showed a shift of the whole curve toward a smaller pore-radius position as acetylation increased up to 14.6%. At higher acetyl contents the predominant pore size (peak position) remained approximately the same, but there was a diminution in volume at each pore-radius position throughout the greater portion of the interfiber and interyarn pore-size ranges. A photomicrograph of the yarn cross section of the most highly acetylated sample (28.2% acetyl) revealed the fact that the fibers had become considerably distorted as they increased in coarseness within the confined spaces of the constricted yarn.

For comparison, this study included two additional fabrics whose constructions were as nearly alike as possible and whose yarns had been spun, respectively, from Iquitos cotton and from Iquitos fibers after partial acetylation in the fiber form to 17.4% acetyl. Though the predominant pore sizes (peaks of distribution curves) of this pair occurred at higher pore-radius positions than those of the sheeting series, the peak shift from the unacetylated to the acetylated was in the same direction and of the same order of magnitude as that for the two comparable members of the sheeting series. The outstanding difference for the Iquitos pair lay in the fact that the void-volume loss was concentrated primarily within the 4–10 μ portion of the interfiber range.

Acknowledgment

The authors are grateful to other sections of this laboratory for their cooperation. The samples were acetylated in the Cotton Chemical Processing Section and the Iquitos pair were made in the Cotton Mechanical Processing Section. The Cotton Fiber Section supplied the density data for Table I and prepared the photomicrograph reproduced in Figure 6.

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Influence of Moisture Sorption and Other Pretreatments on the Acetylation of Cotton with Acetic Anhydride and Pyridine

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TWO different methods have been used for the partial acetylation of cellulose. One of these, acid-catalyzed acetylation, has been the subject of numerous reports [2 through 5, 7, 8, 15, 17, 19] establishing the influence of pretreatments and conditions of reaction in the production of partially acetylated cotton. The other, reaction with acetic anhydride in the presence of pyridine [10], has received less attention. The limited investigations of this reaction which have been reported [1, 9 through 11, 14, 18] indicate the importance of swelling agents in increasing the reactivity of cellulose. However, the influence of moisture sorption and other pretreatments on the acetylation of cotton with acetic anhydride and pyridine has not been systematically investigated. In order to obtain such information, the effect of moisture content and previous sorption history on the extent of acetylation under a selected set of conditions have been studied. The increased reactivity of dried cotton, due to pretreatment with agents other than water, and the reversibility on drying of the effect of treatment with sodium hydroxide, a swelling agent which penetrates the crystalline regions, has also been investigated.

In his discussion of cellulose reactions, Heuser [12] concluded that acetylation is a reaction which exhibits no marked preference for either the primary or secondary hydroxyl groups of cellulose. However, in order for reaction to take place, the reagent must penetrate to the hydroxyl groups. Consequently, the rate of acetylation (or the extent of reaction under certain arbitrary conditions) is a function of the submicroscopic structure. When cellulose absorbs, water swelling occurs as the water penetrates the intermicellar spaces, and the accessibility of the hydroxyl groups to chemical reaction is increased. In order to obtain penetration into the intramicellar spaces, alkalis, organic bases, or other strong swelling agents are required. Whether regarded as amorphous and crystalline or accessible and inaccessible, the duality of submicroscopic structure of cellulose plays an important role in the acetylation of cotton. As a result, changes in reactivity toward acetylation may be regarded as a reflection of changes in the submicroscopic structure of cotton.

Moisture Sorption

Empire, Stoneville 2B, and Rowden 41B cottons were selected to obtain specimens differing in maturity and fineness (Table I). In addition to acetylation of all three raw cottons, the first two were acetylated after purification by successive extraction with hot alcohol and boiling in 1% alkali [13]. The cotton samples were brought to the absorbing side of the moisture sorption cycle by drying them in an oven at 110° C. for 16 hr. and then conditioning them at suitable relative humidities until they had reached the desired moisture contents. The desorbing cottons were prepared by

TABLE I. Fiber Properties of Cottons

Property	Variety: Empire	Stoneville 2B	Rowden 41B
Length			
Fibrograph			
Upper half mean, in.	1.02	1.15	0.98
Uniformity ratio	70	73	80
Suter-Webb array			
Upper quartile, in.	1.19	1.26	1.08
Mean length, in.	0.96	1.04	0.92
Coefficient of variation, %	32	29	26
Strength			
Pressley Index	6.0	7.4	7.8
Fineness			
Micronaire value	3.8	3.6	6.1
Maturity			
NaOH method, %	68	82	92

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soaking the samples in water for 16 hr., after which they were allowed to dry to selected moisture contents by exposure to the atmosphere or in constant-humidity chambers. While no special effort was made to assure moisture equilibrium for each of the samples, reproducible results were obtained for a number of samples conditioned in the same way but for different lengths of time.

Approximately 1-g. samples of the conditioned fibers were soaked in 15 ml. of anhydrous pyridine for 30 min. at 30° C., after which 15 ml. of acetic anhydride was added. The acetylation was allowed to proceed for 3 hr. at 30° C. and was stopped by thoroughly washing the samples with water. The acetyl content was determined on the dried samples using the Eberstadt method as modified by Genung and Mallatt [6].

The results, plotted in Figure 1, demonstrate the striking dependence of the degree of acetylation, not only on the moisture content of the samples, but also on their previous sorption history. Very little reaction takes place with the previously dried raw cottons until they have absorbed about 8 to 10% of moisture, after which the degree of acetylation increases rapidly as the moisture content increases to between 20 and 22%. Further increase in moisture has little effect on the extent of acetylation, essentially constant values of 6.5 to 7.0% acetyl being obtained under the conditions employed for each of the cottons which have absorbed more than 22% moisture. The behavior of the raw cottons which had been soaked in water was quite different. Although the maximum acetylation was the same as

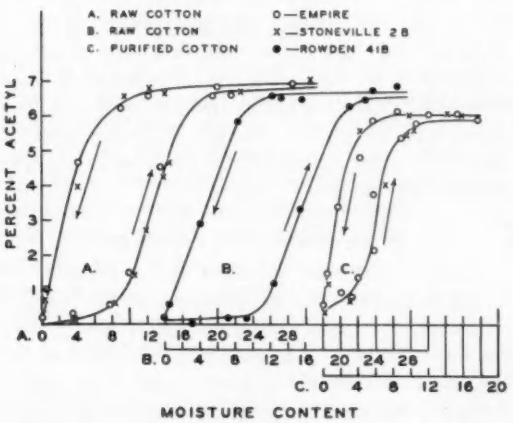

Fig. 1. Influence of moisture content and previous sorption history on extent of acetylation.

that with the absorbing samples, no decrease in reactivity was noted until the moisture content was reduced to about 10%, after which the acetyl content decreased rapidly with loss of moisture.

The results obtained with Empire and Stoneville, cottons of similar fineness but differing in maturity, fall on the same curves (Figure 1, A) for both absorption and desorption. On the other hand the data for Rowden (Figure 1, B), a much coarser cotton, indicate that in the case of both absorption and desorption a higher moisture content is required to achieve a given degree of acetylation, although the maximum extent of acetylation was the same for all three raw cottons. The differences observed may be due to the smaller surface area per gram and the greater diameter of the coarser cotton which requires more extensive swelling for attaining a given degree of accessibility.

The curves for the purified cottons (Figure 1, C) differ considerably from those for raw cotton, although the effect of previous sorption history is readily apparent. The degree of acetylation obtained for the dried purified samples increased more rapidly as water was absorbed and reached a constant value at a substantially lower moisture content. However, the maximum acetylation was slightly lower than that for raw cotton. On desorption the moisture level could be reduced to about 5% without significant reduction in the extent of acetylation, but further drying resulted in a rapid decrease in reactivity. It appears, therefore, that the presence of the noncellulosic constituents in raw cotton increases the moisture requirement for accessibility.

These changes in the extent of acetylation with moisture content and previous sorption history reflect variations in accessibility brought about by alterations in the submicroscopic structure of the cellulose. The effect of sorption of water by cellulose has been discussed by Urquhart [20], Smith [16], and White and Eyring [21]. According to these workers on absorption of water by cellulose, some of the water is more strongly bonded than the rest of the water entering the intermicellar spaces. Thus, when a dry cellulose network is exposed to atmospheres of increasing relative humidity, water is absorbed and swelling occurs. This swelling breaks secondary bonds between the glucose chains, and there is an increase in the amount of strongly bonded water as well as an increase in the total water absorbed. On desorption of wet cellulose, the contractive forces of the network are insufficient to

overcome the forces holding some of the strongly bonded water. Consequently, the collapse of the swollen structure and the re-formation of secondary bonds between the chains is not the reverse of the swelling produced by absorption. The retention of water within the swollen structure during desorption by virtue of secondary bonds, or merely by the laws of probability, prevents the complete collapse of the swollen structure until the anhydrous state is reached. The higher reactivity observed for cotton during desorption from the wet swollen condition is therefore due to greater penetration of the acetylating reagent into the distended cellulose.

Presoaking in Pyridine

Earlier workers [10, 14, 20] had exposed their samples to pyridine for 16 to 48 hr. before acetylation and had not observed the pronounced effect of moisture sorption history which was noted above, using a 30-min. presoak in pyridine. Consequently, a number of conditioned samples of purified Empire cotton were treated with pyridine at 30° C. for selected periods prior to the 3-hr. acetylation in order to investigate the effect of length of presoak.

The data (Figure 2) show that long exposure to pyridine increases the degree of acetylation obtained. Thus, the effect of desorption of moisture or even of moisture content on the extent of acetylation would be obscured. Apparently the accessibility of a dry sample of cotton can be increased by long exposure to pyridine until it shows as much reactivity as a moist sample after a short period of exposure. However, the reactivity of cotton after short exposure to pyridine is greater when it is desorbing moisture and is definitely dependent on its moisture content.

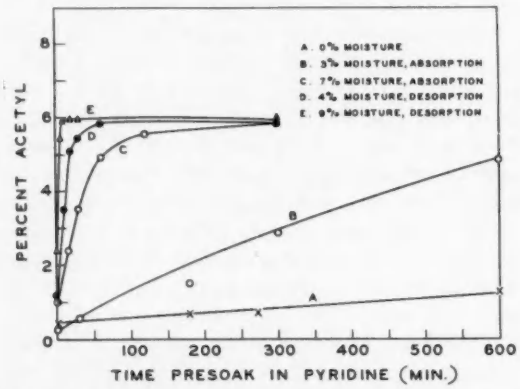

Fig. 2. Influence of length of pyridine presoak on extent of acetylation.

TABLE II. Influence of Pretreating Agents on Acetylation of Cotton

Pretreatment agent	Conditions of treatment*	Acetyl (Moisture-free basis) (%)
None		0.59
Dimethylamino ethanol	24 hr., r.t.	2.27
Pyridine	1 hr., reflux	5.16
Acetic acid	48 hr., r.t.	5.70
Methanol	48 hr., r.t.	5.76
Water	1 hr., reflux	6.14
Dimethylformamide	48 hr., r.t.	6.33
Formamide	48 hr., r.t.	6.63
Ethanolamine	24 hr., r.t.	7.22
Hydrazine, 69.4%	24 hr., r.t.	7.69
Ethylenediamine	24 hr., r.t.	13.10
Propylenediamine	24 hr., r.t.	15.06

* All samples after exposure to the pretreatment agent at room temperature (r.t.) or by refluxing were solvent exchanged with pyridine so that the exposure approximated a 30-min. presoak. No attempt was made to determine the minimum time of pretreatment with the various agents necessary to attain degree of acetylation indicated.

Other Pretreatments

In view of the changes in reactivity brought about by pyridine, the effect of pretreatment with several other liquid agents on the extent of acetylation was also investigated. For this purpose oven-dried samples of Empire cotton were treated under the conditions specified in Table II. The liquid-treating agents were then removed by solvent exchange with pyridine in such a way that the exposure to pyridine approximated a 30-min. presoak. Since it had been found (Figure 2) that this short exposure had little effect on the reactivity of dry cotton, the major part of any effect noted can be attributed to the pretreating agent. From the data tabulated in Table II, it is apparent that a number of agents including organic acids, amides, and amines are able to increase the accessibility of dry cotton to acetylation, but only the organic bases such as hydrazine and the diamines which are generally considered to penetrate the crystalline regions show an effect substantially greater than boiling water.

Swelling with Alkali

It was, of course, expected that treatment with strong aqueous alkalis would increase the reactivity of the cotton toward acetylation, but in order to test the reversibility of the alkali-induced effect on drying, some investigations were made using aqueous sodium hydroxide. Air-dried samples of purified Empire cotton were treated at room temperature with sodium hydroxide solutions of the concentrations

TABLE III. Effect of Drying on the Increase in Reactivity of Cotton on Treatment with Alkali

Concentration of NaOH (%)	Acetyl content (moisture-free basis)	
	Acetylated directly (%)	Acetylated after drying and resoaking in water (%)
5	6.51	6.25
10	7.39	6.74
15	13.26	10.25
20	13.41	10.57
30	14.60	11.67
40	14.94	11.76
50	14.63	12.18

indicated in Table III for 1 hr., then washed thoroughly in water to remove the alkali, solvent exchanged with pyridine and acetylated as specified above. A second series of samples was treated similarly, using the same concentrations of alkali, but oven dried after being washed free of the alkali. These dried samples were soaked in water for 20 hr. and then solvent exchanged with pyridine and acetylated. As was expected, treatment of cotton with 15% and higher concentrations of sodium hydroxide increased the reactivity toward acetylation under the conditions employed. The samples which were dried after the alkali treatment contained somewhat less acetyl than those which were acetylated without drying, but more than when no alkali treatment was used. It seems apparent that treatment with strong alkali increases the accessibility of cotton. An appreciably increased reactivity is still retained after subsequent drying.

Summary

A study of the acetic anhydride–pyridine procedure for acetylation of cotton has shown that the degree of acetylation under specified conditions is not only dependent on the moisture content but also on the previous moisture sorption history of the sample. The data indicate markedly greater reactivity, under the conditions employed, of cotton fibers which are desorbing moisture over those of the same moisture content which are absorbing moisture. Long pretreatment with pyridine increases the reactivity of cottons which are absorbing moisture and so tends to eliminate differences due to previous sorption history. Increased reactivity similar to that produced by moisture can be obtained by using a number of other pretreatments. However, the degree of reactivity produced by high moisture contents could be exceeded only with pretreating agents generally considered to penetrate the crystalline regions of the cotton. It was also found that the increased reactivity produced by treatment with strong aqueous alkali was not completely lost on drying.

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Stress-Relaxation and Vibrational Properties of Some Fibrous Polymers at Various Conditions of Temperature and Relative Humidity

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A contribution from the Chemistry Department of the University of British Columbia, Vancouver, Canada

Abstract

Stress-relaxation curves, dynamic Young's modulus, and dynamic internal friction have been obtained for single filaments of rayon, nylon, and polyethylene at 2° and 25° C. and at several relative humidities. Stress-relaxation measurements have been taken at 0.02 sec. after elongation. Dynamic parameters were observed in a forced longitudinal vibration experiment in which the vibrational frequency could be varied from approximately 5 to 50 cps. It is found that the dissipation of energy per cycle of vibration (measured by $\eta\omega$) increases with increasing relative humidity, but that the slope of the stress-relaxation curve decreases with increasing relative humidity. An indication is given that energy dissipation in viscose rayon is independent of hydrogen bonding in the material.

THE problem of correlating the results of different kinds of experiments on the mechanical properties of polymers—creep, stress relaxation, vibrational studies, etc.—is one of considerable current interest, and such a correlation has been very satisfactorily achieved in many cases through the use of an appropriate form of a distribution of relaxation times to characterize the mechanical behavior of the polymer. Valuable contributions to this area of polymer research have been made by J. D. Ferry and his co-workers and by A. V. Tobolsky and his co-workers over the past ten years or so. Less attention has been paid, however, to fibrous materials than to rubbery and glassy polymers, and little quantitative work has been done on the variation of mechanical properties with temperature and relative humidity changes for fibrous polymers. The investigation reported in this paper was initiated to examine in more detail the applicability to fibrous polymers of the correlation suggested by Tobolsky, Dunell, and Andrews [7] for stress-relaxation and vibrational experiments. Although no satisfactory interpretation has been found for the general pattern of our results, some interesting details of the mechanical behavior of nylon, rayon, and polyethylene filaments are presented here.

Stress Relaxation

Apparatus

Meredith [4] and Watson, Kennedy, and Armstrong [8] have recognized the desirability of obtaining stress-relaxation measurements at very short times after the sample is initially stressed, and they have described apparatuses for achieving this end. In the work presented here we have used two modifications of an arrangement similar to that of Watson, *et al.*, from which we have obtained the first reliable stress-relaxation measurement at 0.02 sec. after stretching the fiber. One modification is illustrated in Figure 1, which shows schematically the mechanical arrangement of the stress-relaxation apparatus, by means of which a specimen fiber, attached at one end to a strain gauge and at the other to a rod and spring, is suddenly stretched by the spring to a predetermined length when a trigger mechanism is released. Figure 2 shows the electrical arrangement in which the d.c. unbalance of the strain-gauge bridge circuit is amplified in a d.c. preamplifier and recorded photographically from the screen of a DuMont model 304 cathode-ray oscilloscope during the first second, and thereafter read from a Rhodes potentiometer-voltmeter. The strain gauges used

were type G1-1.5-350 made by Statham Laboratories, Inc. Calibration of the strain-gauge circuit is done with a set of resistors, R_c, one of which is shown in Figure 2. The inclusion of a calibrating resistor in the circuit corresponds to a change in the resistance of one arm of the gauge network, and hence to the application of a stress to the gauge. The circuit was calibrated after each experiment, and the calibration checked periodically by comparing the response of the circuit in this resistor calibration with the response to standard weights applied to the gauge. The other, first-tried modification of the apparatus used a type of transducer different from the strain gauge. One end of the fiber was connected to the movable plate of a mechano-electronic transducer tube, RCA 5734. The change in plate-cathode voltage, induced by movement of the plate with respect to the cathode as the stress on the sample changed, was observed on the cathode-ray oscilloscope and a vacuum-tube voltmeter. The shortness of the useful life of the transducer tube used repeatedly under maximum load led us to abandon this form of the apparatus.

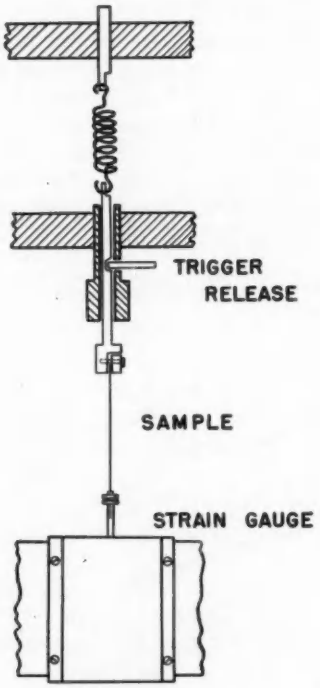

Fig. 1. Schematic diagram of stress-relaxation apparatus.

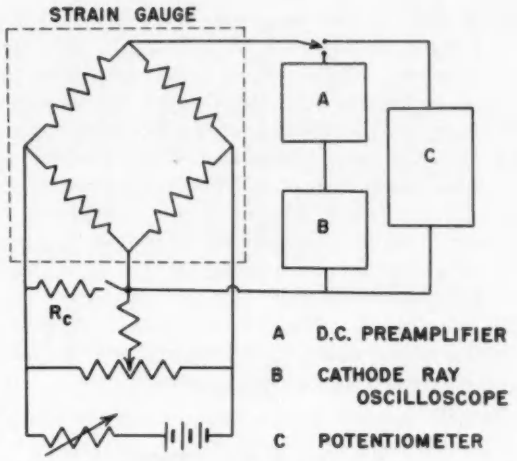

Fig. 2. Electrical circuit for stress-relaxation apparatus.

Experiments were done in a constant-temperature room, controlled to within ±0.5° C. Control of relative humidity was obtained by splitting an air stream and passing one portion through silica gel and the other through a water-saturating column. The dried and saturated air were then mixed in appropriate proportions to give approximately the desired relative humidity, and the mixed stream was circulated through a jacket surrounding the apparatus and test fiber. The relative humidity within the jacket was measured by a wet- and dry-junction thermocouple pair constructed according to the specifications of Powell [5] to be suitable for fairly accurate determination of relative humidity in air streams of very low velocity.

Experiments and Results

Filaments of acetate rayon, viscose rayon, nylon, and polyethylene were examined in stress-relaxation experiments at 25° and at 2° C, both at various relative humidities. In each experiment the mounted specimen was allowed to stand loose in the enclosed apparatus for 4 hr. at the temperature and relative humidity at which the experiment was to be carried out. The fiber was then placed under just sufficient tension to hold it straight, and the conditioning continued for another 16 hr., after which time it was stretched suddenly by releasing the spring and the resulting stress in the fiber observed as a function of time from the oscilloscope and the potentiometer. For any one kind of fiber, the strain did not vary greatly for all experiments with that kind of fiber:

0.020–0.027 for acetate rayon, 0.020–0.030 for viscose rayon, 0.033–0.045 for nylon, and 0.014 for polyethylene. The results of these experiments are shown in Figures 3 through 6 as "stress-relaxation modulus," i.e., stress at time t after stretching divided by the strain, plotted against logarithmic time. In these figures each point represents the average of at least two values obtained in two experiments on separate filaments, no value differing from the mean by more than $0.1(10^{10})$ dynes/cm.^{2}, or in the case of polyethylene, by more than $0.1(10^9)$ dynes/cm.^{2} The time origin for the relaxation curves is considered to be the time at which stretching is finished, which is taken as the highest point on the oscilloscope trace.

Vibrational Experiments

Apparatus

The type of apparatus and the techniques used in the vibrational experiments in this work were the same as those reported by Dunell and Dillon [1], by means of which single filaments were subjected to forced longitudinal vibrations at frequencies in the region of 1 to 100 cps. The vibrating system, consisting of the filaments under test and a transducer, is brought to mechanical resonance by adjusting the frequency of the alternating voltage impressed across the transducer, and at resonance the vibrational amplitude and frequency and the current passing through the transducer are observed. The dynamic behavior of the system can be described by the equation

$$M\,d^2x/dt^2 + R\,dx/dt + Px = F_{\max}\cos\omega t \quad (1)$$

where M is the vibrating mass, x is the displacement of the transducer at time t, and $F_{\max}$ is the amplitude of the sinusoidal applied force driving the transducer at radian frequency ω; and where

$$R = 2A\eta/l + R_1 \quad (2)$$

and

$$P = 2AE_{\text{dyn}}/l + P_1 \quad (3)$$

In Equations 2 and 3, A is the cross-sectional area of the filament, l is the vibrating length of a filament, E_{dyn} is the dynamic modulus, η is the internal friction of the filament, and R_1 and P_1 are small correction factors which have been discussed previously [1].

The experiments were carried out in a constant-temperature room, and relative humidity was controlled and measured as it was in the stress-relaxation experiments, the two portions of the vibrator in which the samples were mounted being enclosed in jackets. The difficulty which this enclosing jacket introduced into clamping the fibers at varying lengths as resonant frequency was changed was overcome by controlling the clamps by magnets acting from outside the jacket.

Experiments and Results

Filaments of acetate and viscose rayons, nylon, and polyethylene were tested in forced longitudinal vibration to determine their dynamic modulus and dynamic viscosity at various relative humidities at both 25° and 2° C. The filaments to be tested were mounted in the vibrator in each experiment and were kept untensioned at the desired temperature and relative humidity for at least 16 hr. After this time a

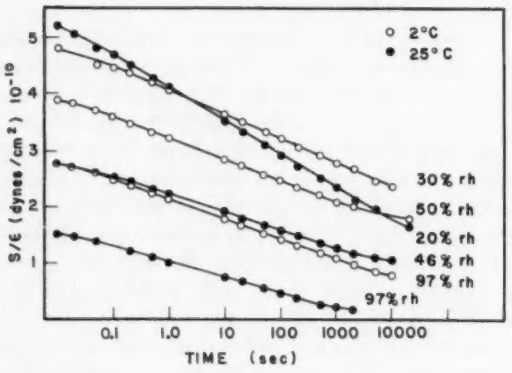

Fig. 3. Stress-relaxation curves for acetate-rayon monofilaments. Strain (ϵ) varies between 0.020 and 0.027.

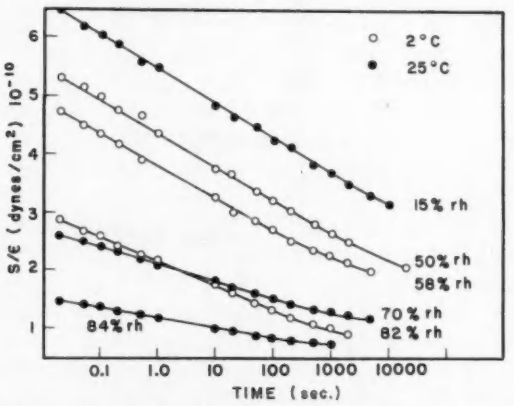

Fig. 4. Stress-relaxation curves for viscose-rayon monofilaments. Strain (ϵ) varies between 0.020 and 0.030.

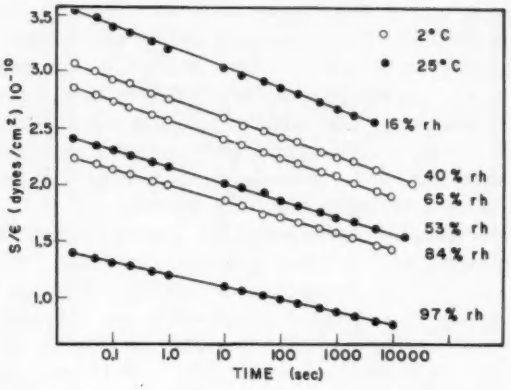

Fig. 5. Stress-relaxation curves for nylon monofilaments. Strain (ϵ) varies between 0.033 and 0.045.

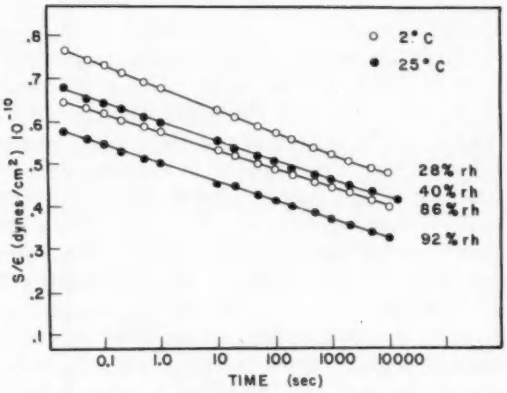

Fig. 6. Stress-relaxation curves for polyethylene monofilaments. Strain (ϵ) is 0.014.

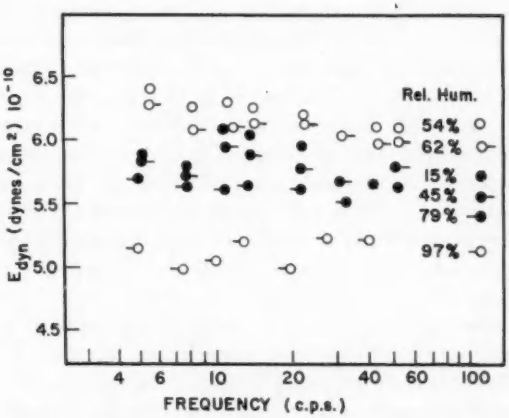

Fig. 7. Dynamic Young's modulus of acetate-rayon monofilaments. Dynamic strain amplitude is $1.8(10^{-8})$. Open circles 2° C., filled circles 25° C.

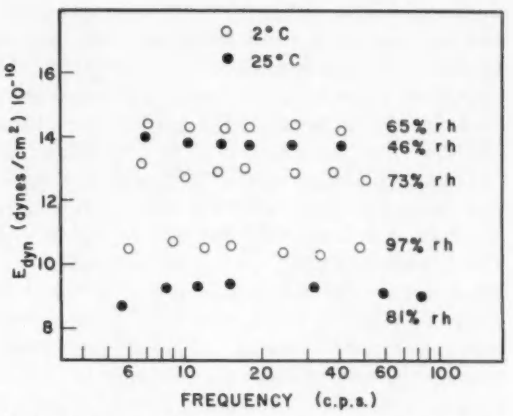

Fig. 8. Dynamic Young's modulus of viscose-rayon monofilaments. Dynamic strain amplitude is $1.5(10^{-8})$.

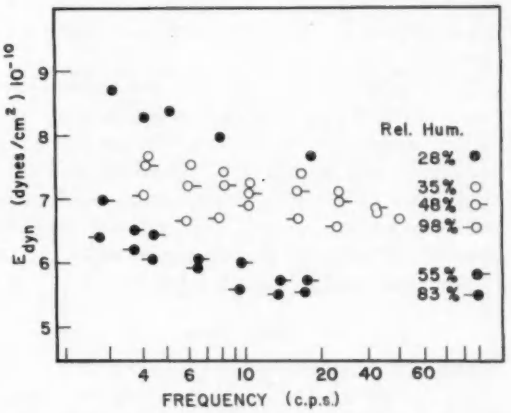

Fig. 9. Dynamic Young's modulus of nylon monofilaments. Dynamic strain amplitude is $2.7(10^{-8})$. Open circles 2° C., filled circles 25° C.

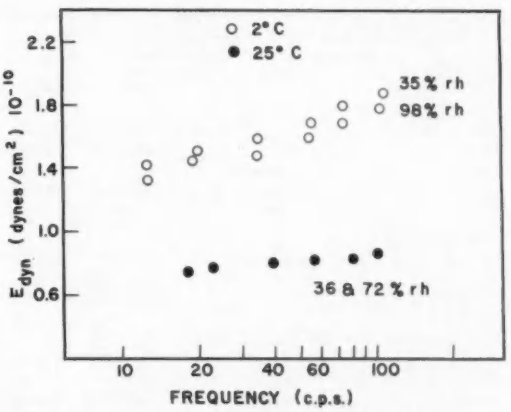

Fig. 10. Dynamic Young's modulus of polyethylene monofilaments. Dynamic strain amplitude is $0.67(10^{-8})$.

tensioning load of 0.5 g./10^{-6} cm.^{2} of cross-sectional area was applied to the filament, and they were allowed to creep under this load for 18 or 20 hr. The vibrational experiments were then performed at dynamic strain amplitudes of $1.5(10^{-3})$ for viscose, $1.8(10^{-3})$ for acetate, $2.7(10^{-3})$ for nylon, and $0.67(10^{-3})$ for polyethylene. The relative humidity was checked periodically during the conditioning periods and was frequently observed during the run. The dynamic moduli at the various atmospheric conditions are shown in Figures 7 through 10 over the frequency range in which vibrational measurements were made, and dynamic viscosities are plotted against frequency in Figures 11 through 14, both on a logarithmic scale. The broken lines in Figures 11 through 14 are drawn with negative slope of unity, representing the relation $\eta\omega$ = constant, through sets of points corresponding to the upper and lower limits of energy loss for the several conditions under which each fiber was tested.

In both vibrational and stress-relaxation experiments single filaments of all materials were used: 36-den. acetate rayon, 30-den. viscose rayon, 15-den. nylon, and polyethylene monofilament 0.012 in. in diameter. The cross-sectional areas of the rayons and nylon were calculated from the denier and densities of 1.33 g./cc. for acetate rayon, 1.50 g./cc. for viscose rayon, and 1.14 g./cc. for nylon [3].

Discussion

Although the stress-relaxation values we have obtained for the rayons cannot be compared directly with those of Meredith [4] because of differences in conditions under which experiments were done, we have made a rough interpolation to reduce our values to 20° C. and 65% humidity and another to find a value from Meredith's results which will correspond to a strain of approximately 0.025, as used in our experiments. The estimated comparison is indicated in Table I, which shows that agreement is within about 20%. It is somewhat surprising that our values agree better with those Meredith obtained for mechanically conditioned fibers than with those he obtained from the first relaxation of a fiber. This state of affairs may perhaps be explained by the small amount of mechanical conditioning our specimens were given in the period preceding the final stretching. After being mounted loosely for 4 hr., the fiber was put under 3 or 4 g. tension and allowed to continue in contact with air of the desired temperature and relative humidity. At the end of the conditioning period, the recording instruments were set to zero at the residual stress remaining in the fiber and the fiber then was stretched suddenly to the predetermined strain for the experiment. Our results agree quite well with those of Meredith and of Watson [8] in indicating that the stress-relaxation curve for textile materials at ambient conditions is nearly linear on a logarithmic time base over several decades of time down to about 0.01 sec. For all the types of fiber studied, the first recorded stress-relaxation modulus increases with decreasing relative humidity and with decrease in temperature. Similarly the negative slope of the linear part of the stress-relaxation curves increases with decreasing relative humidity. It is not clear, however, whether the negative slope necessarily increases with decrease in temperature.

TABLE I. An Estimated Comparison of Stress-Relaxation Values from This Work with Those of Meredith [4] for Acetate and Viscose Rayon

		Meredith's work	
	This work dynes/cm^2	1st Relaxation dynes/cm^2	2d Relaxation dynes/cm^2
Acetate rayon			
$(S/\epsilon)_{t=0.1\text{ sec.}}$	$2.4(10^{10})$	$3.2(10^{10})$	$2.8(10^{10})$
$-\frac{d(S/\epsilon)}{d \log t}$	$0.31(10^{10})$	$0.36(10^{10})$	$0.27(10^{10})$
Viscose rayon			
$(S/\epsilon)_{t=0.1\text{ sec.}}$	$3.0(10^{10})$	$4.0(10^{10})$	$3.5(10^{10})$
$-\frac{d(S/\epsilon)}{d \log t}$	$0.35(10^{10})$	$0.65(10^{10})$	$0.42(10^{10})$

Although the results of the dynamic experiments are more scattered than those of the stress-relaxation experiments, some well-defined trends can be seen. The energy loss per cycle in all the materials, as measured by the product $\eta\omega$, decreases with decreasing relative humidity, though again with decrease in temperature it is not clear whether $\eta\omega$ necessarily increases. The dynamic modulus increases with decreasing relative humidity and with decrease in temperature. The higher sensitivity of the dynamic modulus of viscose to change in relative humidity compared with that of acetate may be attributed to the greater extent of hydrogen bonding in viscose. The fact that the energy loss in viscose changes very little with change in relative humidity suggests, however, that hydrogen bonding is not of great consequence in

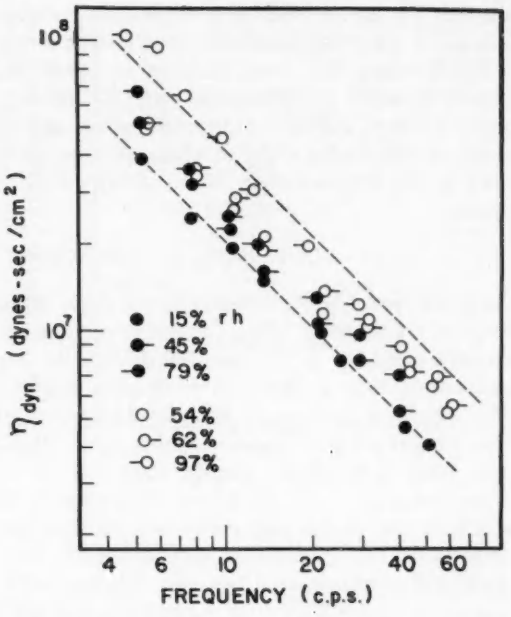

Fig. 11. Dynamic viscosity of acetate-rayon monofilaments. Open circles 2° C., filled circles 25° C. Broken lines represent $\eta\omega =$ constant.

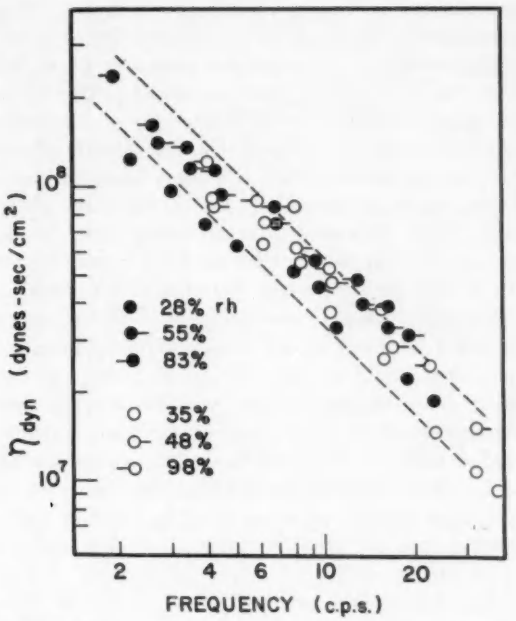

Fig. 13. Dynamic viscosity of nylon monofilaments. Open circles 2° C., filled circles 25° C. Broken lines represent $\eta\omega =$ constant.

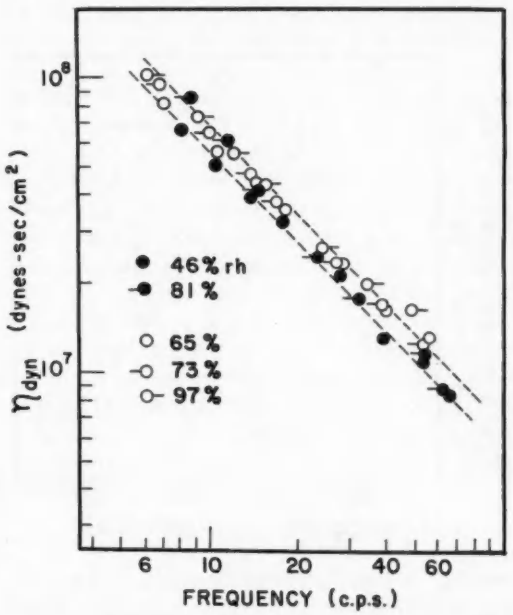

Fig. 12. Dynamic viscosity of viscose rayon monofilaments. Open circles, 2° C., filled circles 25° C. Broken lines represent $\eta\omega =$ constant.

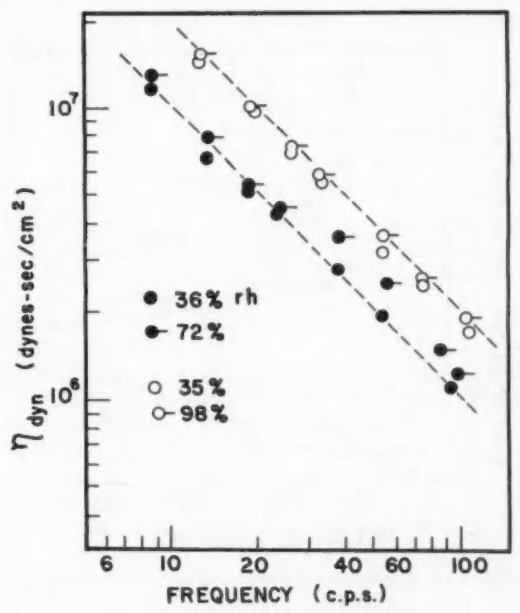

Fig. 14. Dynamic viscosity of polyethylene monofilaments. Open circles 2° C., filled circles 25° C. Broken lines, represent $\eta\omega =$ constant.

the mechanism of energy loss in viscose rayon. This conclusion is supported by the evidence that the activation energy for the molecular processes associated with the dispersion of modulus and of $\eta\omega$ of viscose at temperatures near $-50°$ C. is only of the order of 1 kcal./mole [2]. Tipton [6] has recently shown that the dynamic modulus increases markedly with increasing static strain imposed on the fibers under test. Since the extent of creep taking place during the conditioning period when the fiber is loaded with 0.5 g./10^{-6} cm.^{2} cross-sectional area will increase as the relative humidity increases, the modulus values recorded here are larger at the higher humidities than they would be had they been observed at the static strain imposed on the samples tested at low humidities. For a given type of fiber, then, dynamic moduli should be expected to show a greater spread with relative humidity change than that indicated in this paper if they were measured at constant static strain. It is not probable that this effect would account for the difference in the behavior of viscose and acetate rayons, however. Examination of Tipton's results indicates that within the probable limits of the static strains involved (0.02–0.10) the change in dynamic modulus with static strain is not large, nor is it of very different character in acetate and viscose. Tipton has found that the change in energy loss, $\eta\omega$, is not greatly dependent on the static strain.

Some success has been achieved in correlating stress relaxation and vibrational data for fibers by use of a "step" distribution function which, applied to an infinite parallel array of Maxwell visco-elastic units as the representation of the fiber, gives the equation

$$\eta\omega = (-d(S/\epsilon)/d \log_{10} t)\,\pi/4.606 \qquad (4)$$

where the factor in the brackets is the slope of the linear part of the stress-relaxation curve on a logarithmic time plot [7]. It must be admitted that the step function predicts an increase in dynamic modulus with increasing frequency, in contradiction to the experimental evidence presented in this paper. However, until a more satisfactory interpretation of stress-relaxation and vibrational experiments is found, the use of the step distribution function remains as the best explanation for the observed magnitude and constancy with frequency of energy dissipation in a wide variety of materials. Meredith's results, showing that the slope of the stress-relaxation curve increases (numerically) with decreasing strain on the fiber, point to generally improved agreement in reference [7] between observed energy loss

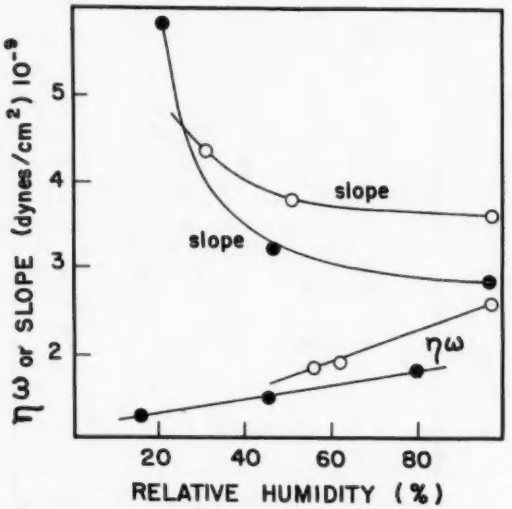

Fig. 15. A comparison of the variation with relative humidity of the slope of the stress-relaxation curve $\left(-\frac{d(S/\epsilon)}{d \log t}\right)$ and the factor $\eta\omega$ for acetate rayon. Open circles 2° C., filled circles 25° C.

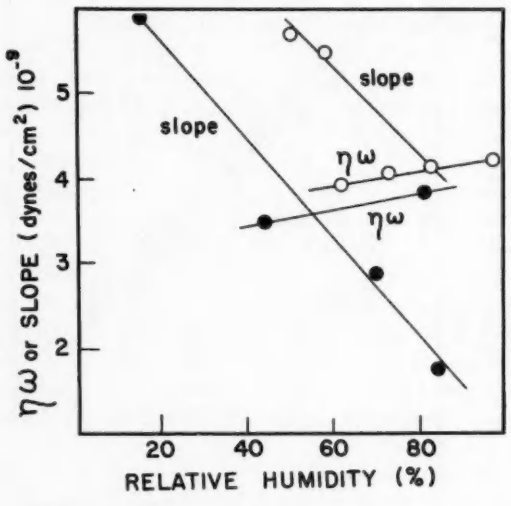

Fig. 16. A comparison of the variation with relative humidity of the slope of the stress-relaxation curve $\left(-\frac{d(S/\epsilon)}{d \log t}\right)$ and the factor $\eta\omega$ for viscose rayon. Open circles 2° C., filled circles 25° C.

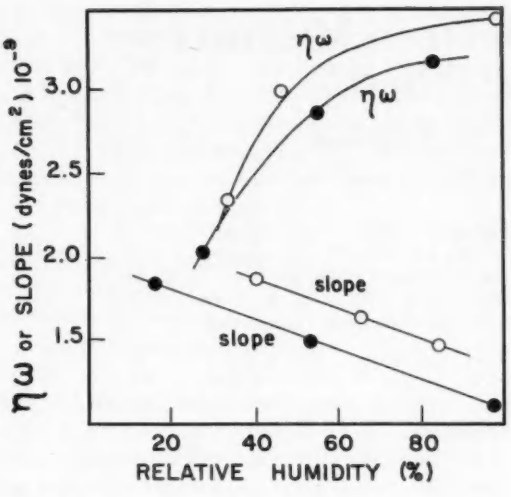

Fig. 17. A comparison of the variation with relative humidity of the slope of the stress-relaxation curve $\left(-\frac{d(S/\epsilon)}{d\log t}\right)$ and the factor $\eta\omega$ for nylon. Open circles 2° C., filled circles 25° C.

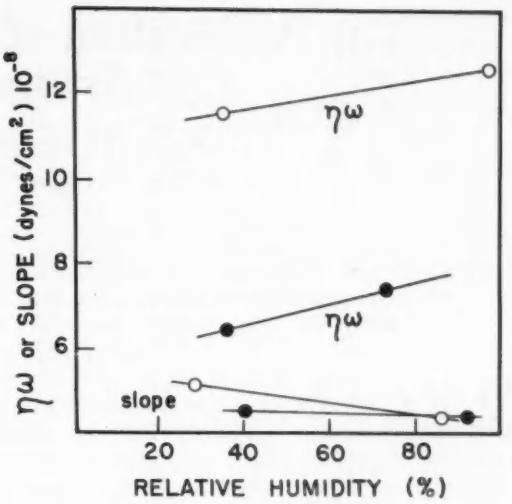

Fig. 18. A comparison of the variation with relative humidity of the slope of the stress-relaxation curve $\left(-\frac{d(S/\epsilon)}{d\log t}\right)$ and the factor $\eta\omega$ for polyethylene. Open circles 2°C., filled circles 25° C.

and that calculated from the slope of the stress-relaxation curve. The dynamic strains involved in the vibrational experiments are much smaller than the strains used in the stress-relaxation experiments, and therefore larger values of the slope of the stress-relaxation curve corresponding to smaller strains are appropriate for calculating energy losses.

The slopes of the stress-relaxation curves and the values of $\eta\omega$ are shown in Figures 15 through 18 at 25° and 2° C. at various humidities for the fibers tested. The fact that $\eta\omega$ increases with increasing relative humidity whereas the slope of the stress-relaxation curve decreases, contrary to the prediction of Equation 4, has not been explained. It is perhaps important that whereas the fibers which are used in the vibrational experiments have been given a mechanical preconditioning in the form of a 20-hr. creep period, those fibers which are used in the stress-relaxation experiments have not had such a severe pretreatment.

Acknowledgments

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The Application of Electron Microscopy to Synthetic Fibers[1]

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A review of present electron microscope techniques used in the study of synthetic fibers is presented. These include surface replication and ultrathin sectioning. A new method is introduced in which the region to be studied is made insoluble either by chemicals or 60 kv. electrons and then the unaffected region is removed by solvents. The application of this technique to surface or internal fiber structure is reported.

WITH the introduction of the electron microscope to industrial research in the late 1930's, attempts were made almost immediately to apply the instrument to the problem of physical characterization of textile fibers. It is beyond the scope of this report to do more than outline the effort to gain useful information in that field. Many good reviews of the special techniques involved have been published [6, 8]. These special methods are required principally because of the limiting thickness of samples capable of such study.

Attention was first turned to techniques that involved partial disintegration of the fiber before observation. Barnes and Burton [2] were first to show a direct comparison of results obtained from this technique, when applied to the electron microscope and to the light microscope. In their study, cellulose fibers were fragmented in a Waring Blendor. In more recent work Wuhrman, Heuberger, and Muhlethaler [20] have shown that ultrasonic treatment can produce the same effect. Useful information concerning the particulate or fibrillar nature of the sample can be obtained by this technique, but one cannot tell how such components are organized or where they are located in the fiber.

Barnes, Burton, and Scott [3] modified a technique of Heidenreich and Matheson [9] to allow observation of fiber surface structure. The technique involved the production of a plastic replica of the surface from which a thin, positive, silica replica was produced. This method has been widely used and modified. Replicas of more uniform quality have been produced by single-step evaporation methods [14], and contrast in detail was improved by the introduction of the shadow-casting techniques of Williams and Wyckoff [19].

These techniques have recently been used to gain information concerning the interior structure of fibers. Cobbold, Daubney, Deutsch, and Markey [4] have shown longitudinal fibrillation in polyethylene terephthalate monofils that had been split along their long axis followed by replication of the freshly produced surface. Kassenbeck [13] has shown that by polishing cut ends of fibers, variations in hardness of the skin and core can be revealed by proper replication. Peck [17] has demonstrated that solvent etching can be used, as it is in metallurgy, to produce or enhance surface structures.

At the same time that replica techniques were being developed, attempts were underway to extend methods used to produce thin sections for light microscopy so that they might be used in electron microscopy to show internal structures by direct observation. The problem was one of cutting samples one-tenth as thick as the thinnest sections useful for the optical microscope. Von Ardenne [1] proposed to cut wedge-shaped sections and look for areas thin enough for electron penetration. This gave only specimens having very limited useful areas. For a while attention was turned to a suggestion of O'Brien and McKinley [15] who proposed that thin sections might be produced by cutting at a speed greater than the rate of propagation of the shock wave produced in cutting. In this way it was hoped to remove the section from the block before the shock wave could produce any distortion. High-speed microtomes were developed, and useful information was gained from the sections they produced. However, the apparatus was quite elaborate and expensive, and it was difficult to obtain reproducible results.

[1] Contribution from the Textile Fibers Department, Pioneering Research Division.

Special modifications of biological microtomes by Pease and Baker [16] now allow sections to be cut having useful thicknesses ranging from 0.05 to 0.1 μ. A few articles have been published demonstrating the application of this technique to textile fibers [18, 12]. These indicate that much of the structure observed is on the section surface and can be enhanced by metal shadowing.

Before discussing the further application of the instrument to the characterization of fibers, it will aid in understanding results gained from micrographs and the limitations imposed on samples used, if a few fundamental principles are discussed. In the light microscope, a number of effects have been used separately or in combination to render an object visible to the eye. These include light absorption, scattering, differences of thickness, and differences of refractive index. In the electron optics, image differences are produced only by scattering, which in turn is related to differences in the number of scattering centers. These variations are produced by changes either in specimen thickness or in the atomic number of the scattering materials. The greater the thickness or atomic number, the larger the fraction of the beam that does not reach the fluorescent screen to produce an image. However, not only is there a loss of intensity when observing a thick sample, but also there is a loss in resolving power since the electrons suffer many collisions when passing through the sample and produce a diffuse image.

Additional difficulty is encountered with sections or specimens thicker than 0.1 μ due to thermal effects produced in the sample by electron absorption. Scattering of the electron beam by the specimen results in a local temperature rise that is produced by the conversion of kinetic energy of the electron into heat.

On the other hand, a sample may have irregularities in it which one wishes to view, but the preparation is so thin and of such uniform electron scattering power that no details can be seen in the image. The shadowing technique, devised by Williams and Wyckoff, in which the preparation is subjected to a stream of evaporated heavy metal incident on the sample at an oblique angle in a high vacuum, is then frequently useful. The metal builds up on surfaces toward the metal source, and none is deposited on surfaces whose normals are oriented at angles greater than 90° to the metal beam. When such a preparation is viewed in the electron microscope, these latter regions will pass electrons as freely as they did before the shadowing treatment. On a positive print of such a field these regions will appear as white shadows. For this reason micrographs of shadowed preparations are conventionally printed as negatives. The regions whose normals form angles from 90° to 0° with the metal stream will be increasingly darker in contrast, due to the increased quantities of metal that have been deposited on them. Thus, the preparation will not only show up bumps or pits because of their shadows, but also variations in curvature as variations in gray or as differences in density.

In the observation of preparations in the electron microscope more than in optical microscopy, one has to decide beforehand whether one wishes to study the surface or internal structure of the sample. However, this still does not dictate what techniques should be used. Only when it has been decided what general types of structures are to be observed and what their chemical and physical properties are, can one properly choose the method that will supply the desired information. Before techniques were available in the study of intact fibers, useful information concerning the physical structure of fibers was derived from partial disintegration of the fibers by mechanical means. Micrographs of these preparations showed that the fibers had been split into many fine fibrils with surprising uniformity in their diameters, ranging around 100 A (0.001 den.). There was also fine granular material present as shown in Figure 1, which is an ultrasonically treated sample of Orlon[1] acrylic fiber. Little is known of the internal structure of these fibrils. However, some recent work of Hess and Mahl [11] has indicated a large, long-range periodicity of about 150 A in fibers of polyvinyl alcohol. To render these structures visible, they treated a partially disintegrated fibril with an iodine solution. Because this material had higher atomic number than the elements that went into making up the polymer, it produced dark regions everywhere it had reason to concentrate in the fibrils. In these preparations, Hess suggests that the localization takes place in amorphous regions between crystallites.

In the past, much useful information has been gained from the electron microscopy of intact fibers by using various methods for examining the outer surface of the fibers. This study has been accomp-

[1] Du Pont trademark.

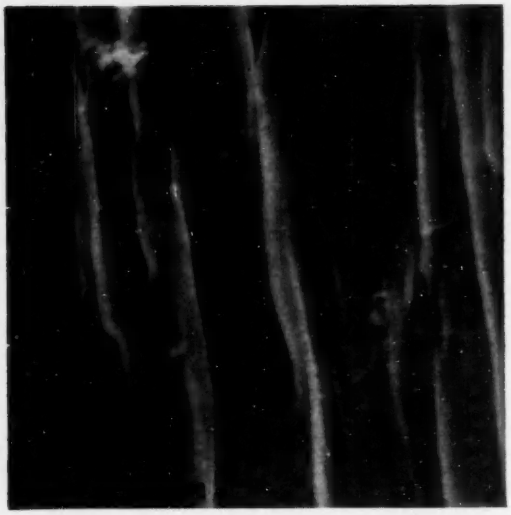

Fig. 1. Fibrils from ultrasonically treated Orlon acrylic fibers.

lished in two general ways. In one, the fiber is molded in a thin film of plastic material; then after suitable treatment, this reproduction is transferred to the microscope for study. The method, although it has an ability to copy structures in size ranges below 100 A, has the serious limitations that replication may be very uneven and only limited areas are copied. Furthermore, distortions are easily produced in the plastic polymer and may be hard to distinguish from real structures. The fact that only limited areas are reproduced does have the advantage that it is easier to control the angle of the shadows. This effect will be discussed later.

In the other method, the reproduction is produced by evaporating inorganic material onto the fiber surface in a high vacuum and observing this film after the fiber is removed mechanically or by solvents. This method produces replicas of uniform quality, representing approximately one half the fiber diameter, that are relatively free from artifacts and may be self-shadowed. That is, the material that produces the replica may be evaporated at an angle to the fiber, thus producing variations of film thickness about elevations and depressions on the fiber surface.

It should be pointed out that shadowing of a fiber surface or a thick plastic replica of the surface has one great difference from the shadowing of spherical dispersion particles mounted on a flat film. In the latter case, the shadowing angle, and hence the relative shadow length, is constant over the entire specimen, while in shadowing a fiber the shadow angle changes from 0° to 90° in one plane. As a result of this, structures in one region may stand out in sharp relief while in other areas, though the same structures exist on the fiber surface, they are not visible. That is, the surface appears smooth, since the shadowing angle in that region was normal to the surface. We have found that these regions can be studied by tilting the sample in the microscope. When the axis of the microscope is parallel to the direction of shadowing, the electron beam will pass through a uniform amount of metal, producing an image of uniform density. However, tilting the sample will produce electron path lengths through the sample of varying distances, as illustrated in Figures 2 through 4. In Figure 3 the sample is normal to the beam, while in Figure 4 it has been tilted to about 20°. The phenomenon was recently reported by other microscopists [5].

The replica techniques have been used to characterize fiber surfaces and to study the effects of

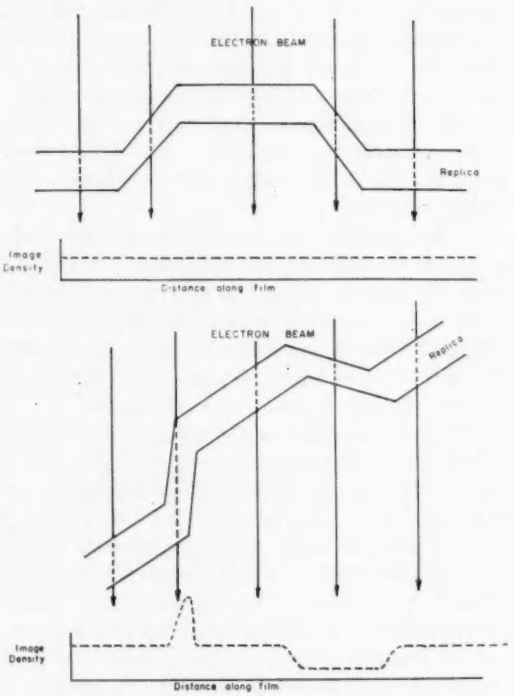

Fig. 2. Diagram to show change in electron path length through a replica when sample is tilted in electron microscope.

chemical and physical agents on them. Figure 5 shows a replica made by carbon evaporation onto a nylon fiber surface. Spherulite structures can be seen separated by lines similar to the grain boundaries observed in metallurgical samples. Figures 6 and 7 show the effect of drawing on an Orlon acrylic fiber. Principal changes are the production of the elongated ridges and unidentified structures, some of which may be cracks in the fiber surface. These structures will be discussed later when we talk about chemical sections.

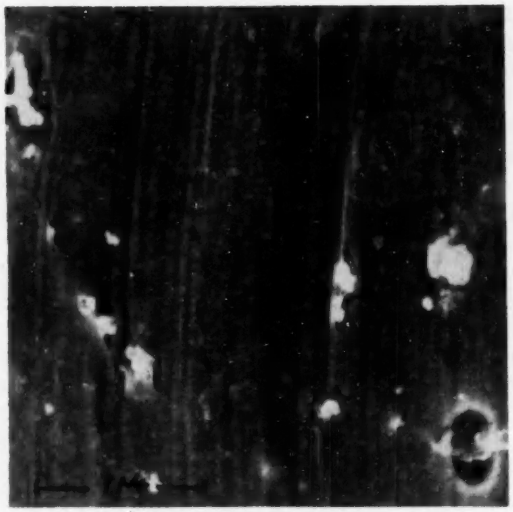

Fig. 3. Replica of Orlon acrylic fiber, surface normal to electron beam.

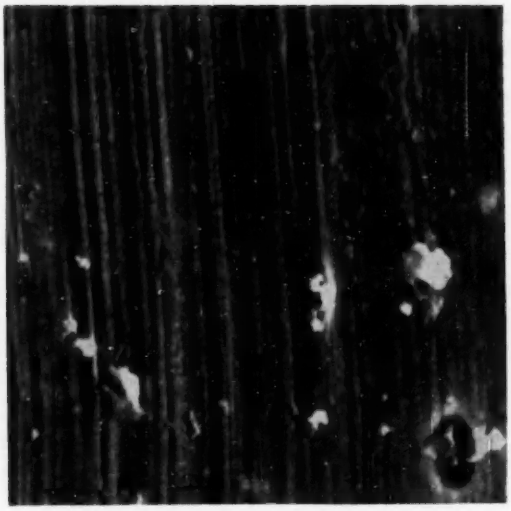

Fig. 4. Same area of the replica shown in Figure 3 tilted about 20° in electron microscope.

However, this method does not give all of the information that one would like to have concerning a fiber surface. For example, often bumps will be observed in a replica of a fiber surface, such as Figure 5, where it is difficult to tell whether these structures are irregularities in the polymer, or pigment, or delusterant particles in the fiber surface.

A new approach to surface studies has recently been found in our laboratory which, among other features, circumvents this limitation. We have devised a technique in which a limited thickness of a fiber surface is made insoluble either by chemical agents or by ionizing radiation. After the soluble portion of the fiber has been removed, the affected portions can be studied directly. This preparation is called a surface section. Fibers made from polyacrylonitrile, for example, have been treated with hot sodium hydroxide solution, then washed in hot dimethylformamide to produce an insoluble film that reveals structures on and in the fiber surface. In this procedure the sample was mounted on glass slides and kept moist with a 20% solution of sodium hydroxide in water while they were heated under an infrared lamp for 30 to 45 min. The sample was then rinsed with water, dried, and washed with hot dimethylformamide. The resulting surface sections

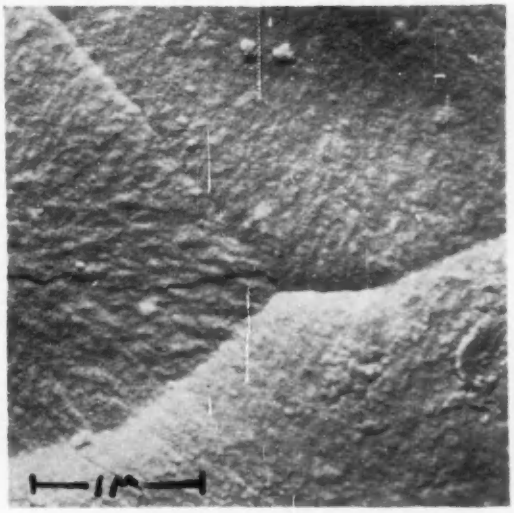

Fig. 5. Carbon replica of nylon fiber surface.

were transferred to Formvar [2] covered screens. Ultrathin, cross or longitudinal, sections of Orlon acrylic fibers were prepared from the surfaces of thick (5 μ) sections or split fibers by the treatment described above.

Sections prepared by this technique are extremely thin. Though no direct measurement has been made, the thickness has been estimated to be about 100 A from comparison of the electron-scattering power of the sections to that of the supporting film. These thin sections result from the poor penetration of the sodium hydroxide into the fiber. The inability of the reagent to penetrate the polymer is the main requirement to be met by insolubilizing agents for other types of fibers. We have named this technique Chemical Sectioning. Fine structures can be studied by shadowing the preparation after it has been treated with the solvent. However, gross structures may be lost by flattening out of the film before shadowing. To retain these structures, the fiber should be shadowed before it is washed with the solvent. On the other hand, if high magnification studies are to be made, these larger structures will not show up in the field of the microscope, and shadowing after treatment with the solvent may offer certain advantages. Among these advantages is the fact that one has a possibility of looking at the actual fiber surface or at structures immediately beneath it. For example, Figure 8 shows a surface section of Orlon. The typical grooves in the surface are clearly visible. The section compares favorably with the polystyrene replica shown in Figure 9. Note that other than the grooves, the surface is relatively structureless. Occasionally we have found specimens which appear to be the shadowed undersurface of the chemical section, such as shown in

[2] Trademark for Shawinigan polyvinyl formal.

Fig. 6. Polystyrene replica of undrawn Orlon acrylic fiber surface.

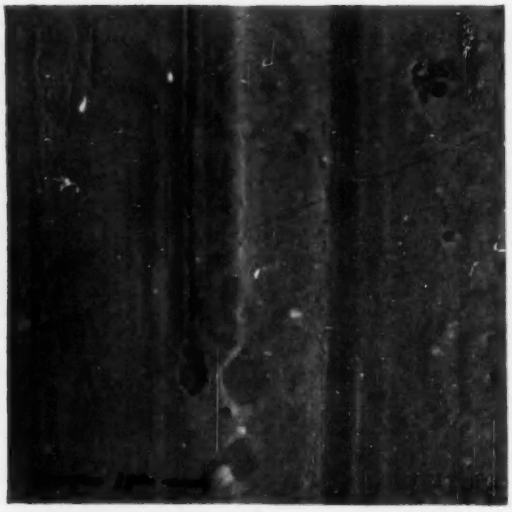

Fig. 7. Polystyrene replica of Orlon acrylic fiber surface (fiber drawn 4×).

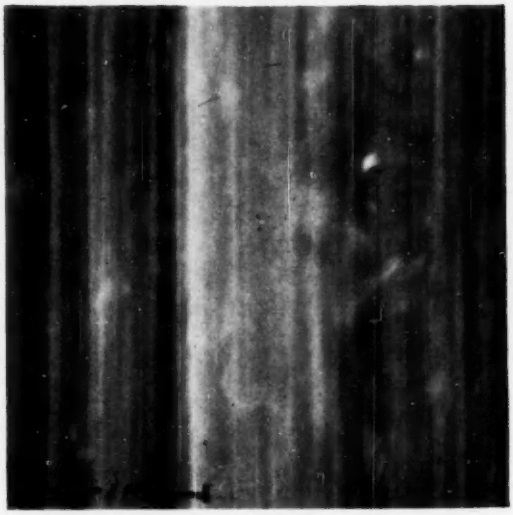

Fig. 8. Chemical surface section of Orlon acrylic fiber surface.

Figure 10. Here a fine granularity can be seen and also coarse structures thought to be derived from cracks in the fiber surface. These chemical sections have an advantage over mechanically cut sections in that they are free of compression distortions.

The technique is also useful in showing the dispersion of pigment in a fiber surface, as seen in Figure 11. Since the preparation was shadowed before solvent treatment, we are looking at the outer portion of the fiber and any particles that have shadows associated with them have caused irregularities in the fiber surface.

This technique of chemical sectioning has not been applicable to all synthetic fibers. In the case of certain fibers, we found that this insolubilizing could be produced by radiating the fibers with the electron beam in the microscope.

A short length of a single fiber is mounted on a glass slide and exposed to the electron beam of the Philips EM-100 microscope at maximum intensity. The treatment is carried out at 60 kv. and 500× for 45 min. It is known that under these conditions samples are at least partly degraded. Next the treated fibers are washed with a proper solvent in order to dissolve the unaffected material in the core, leaving a thin insoluble skin. The resulting preparation is called a radiation section. The effect of the radiation is thought to be a partial decomposition although its exact nature is not well understood. Figure 12 is a radiation surface section of Dacron[3] polyester fiber. This was a control sample to show the introduction of structures to a fiber surface when the polymer was degraded by chemical treatment, as illustrated in Figure 13. This technique has been applicable to Dacron polyester fiber, cellulose acetate, and rayon. The method cannot be used for polymers that are cross-linked by radiation.

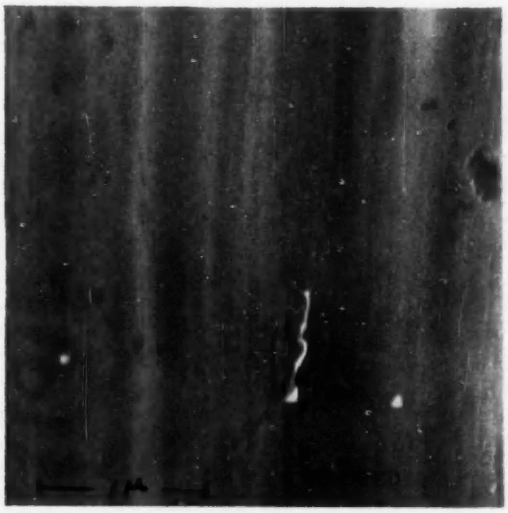

Fig. 9. Polystyrene replica of Orlon acrylic fiber surface.

[3] Du Pont trademark.

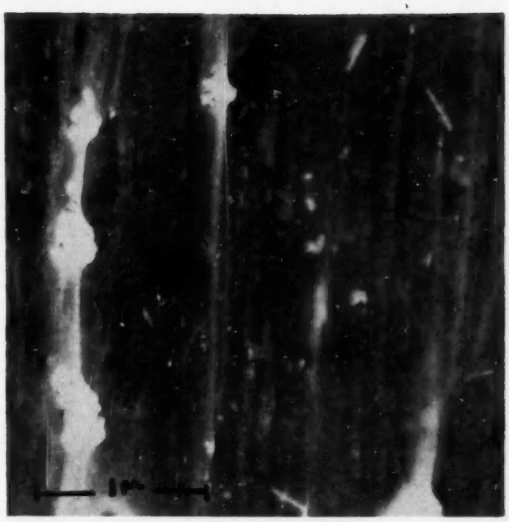

Fig. 10. Underside of chemical surface section of Orlon acrylic fiber.

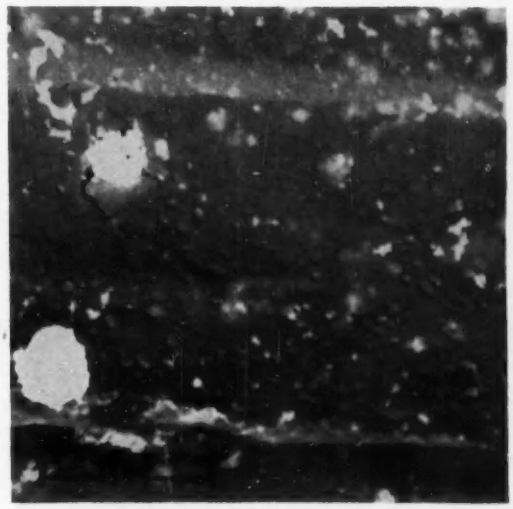

Fig. 11. Radiation surface section of pigmented cellulose acetate fiber.

The techniques just described give information about the outer portion of a fiber. The study of structures within a fiber with an electron microscope requires the production of at least one fresh surface because of the poor penetrating power of the electron beam. Cobbold, et al. [4] have split a large denier filament of polyethylene terephthalate and replicated the cleaved surface. With this technique they were able to show a coarse fibrillar structure. The technique is of interest because of the unusual way of producing this fresh surface, but too little work has been published to measure its usefulness. Kassenbech [13] has cut thick cross sections of embedded fibers, polished the cut ends as one would a metallurgical sample, then replicated the resulting surfaces. Because of differences in hardness between the skin and the core of a cellulose fiber, he was able to show these structures in his replicas. However, the resolving power of the technique seemed to be only slightly better than that obtained with a light microscope.

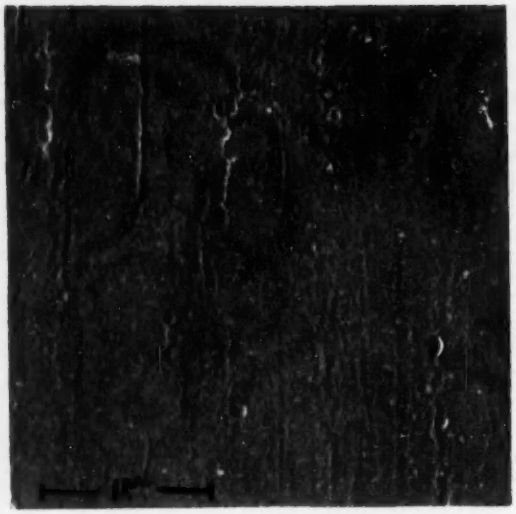

Fig. 12. Radiation surface section of Dacron polyester fiber.

The more direct technique is to produce sections of less than 0.1 μ in thickness and to study them directly under the electron microscope. In the existing literature on these ultrathin sections of fibers, that is, sections of a thickness of 0.1 μ or less, only two recognizable structures have been shown [7, 10, 12]. The air spaces in rayon can be seen in a more or less distorted state, while other micrographs show a region of greater electron scattering power in the outer edge of a fiber than that in the center of the section. This is probably due to a difference in section thickness or density. Figure 14 illustrates this effect observed in an experimental cellulose acetate yarn, sectioned in our laboratory. The difference in skin and core may be easily observed. This preparation is shadowed, and one has essentially a surface replica. Since the chromium used has a much greater electron-scattering power than the polymer, one is looking at the chromium coat rather than the

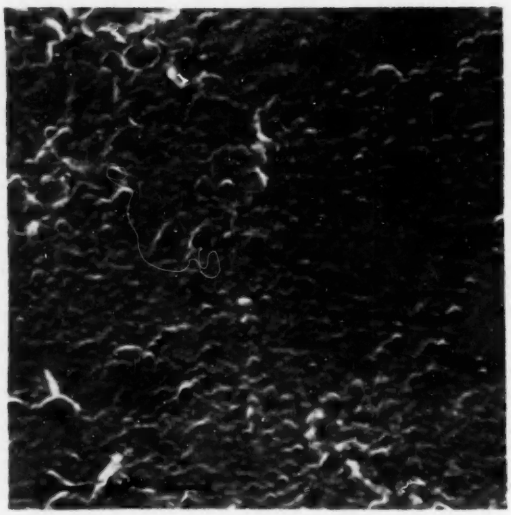

Fig. 13. Radiation surface section of Dacron polyester fiber treated with NaOH.

Fig. 14. Ultrathin longitudinal section of cellulose acetate fiber showing skin-core.

section itself. This replicated-section technique has not only the advantage of added strength from the supporting section, but also the technique can yield information that cannot be gained by true replication. For example, in a section of a fiber made from a mixture of noncompatible polymers, the contribution of the various components can be identified by extraction of the section with selected solvents before the sample is studied. Figure 15 shows a longitudinal section of a fiber made from a mixture of two polymers by dry spinning a homogeneous solution of them. The polymer separation which occurred during spinning is clearly evident. Figure 16 shows the fiber section after removal of one polymer from the fiber section. Figure 17 shows a micrograph of a similar section after removal of the other polymer.

In another fiber made similarly from a 50/50 mixture of two other polymers, shadowing was

Fig. 15. Ultrathin longitudinal section of fiber made from a polymer mixture.

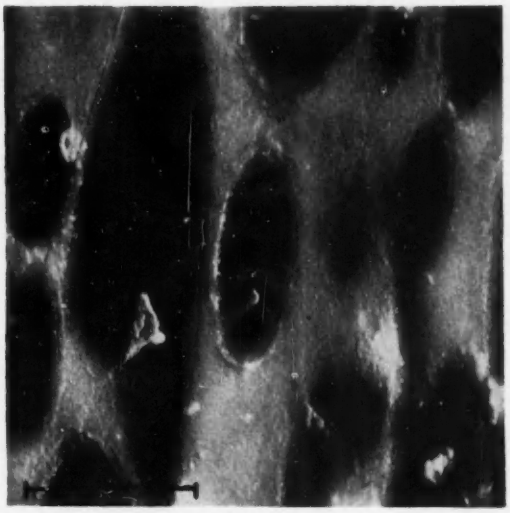

Fig. 17. Same as Figure 15 with second phase removed by a solvent after sectioning.

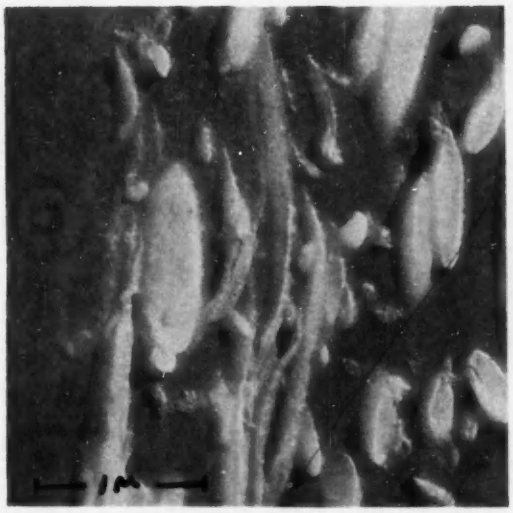

Fig. 16. Same as Figure 15 with one phase removed by a solvent after sectioning.

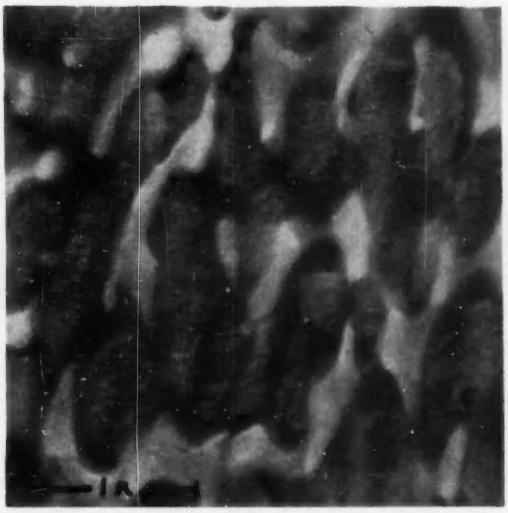

Fig. 18. Ultrathin longitudinal section of fiber made from a polymer mixture showing image contrast developed by different electron-scattering power of the two phases.

superfluous since contrast was produced when the softer components suffered greater compression during sectioning (Figure 18). The polymer separation is seen to be on a much smaller scale in Figure 19 which is a longitudinal section of a fiber made from a 50/50 mixture of cellulose acetate and another polymer. In another instance, ultrathin sections were used to show fibrillar structures and the presence of air spaces in a rayon fiber (Figure 20). The fine unsupported structures in these areas would be very difficult to replicate.

On the other hand, mechanically cut sections have one serious disadvantage. At the time of sectioning, structures may be introduced into the samples which are difficult to distinguish from characteristic polymer structures, and structures may be obscured that one wishes to observe. Figure 21 shows a rodlike structure seen in a longitudinal section of Orlon acrylic fibers that were thought to be characteristic of that polymer until it was observed that these were always oriented at right angles to the direction of movement of the knife. This chatter

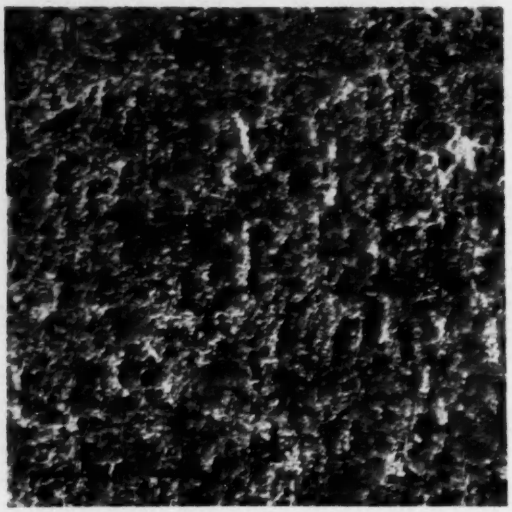

Fig. 19. Ultrathin longitudinal section of fiber made from a polymer mixture showing good compatibility between phases.

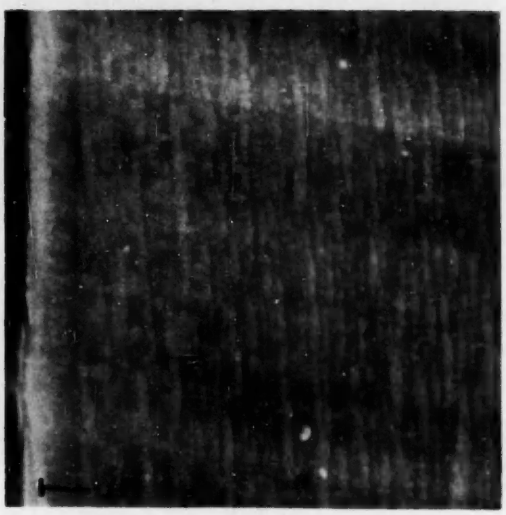

Fig. 21. Ultrathin longitudinal section of Orlon acrylic fiber.

Fig. 20. Ultrathin longitudinal section of viscose fiber.

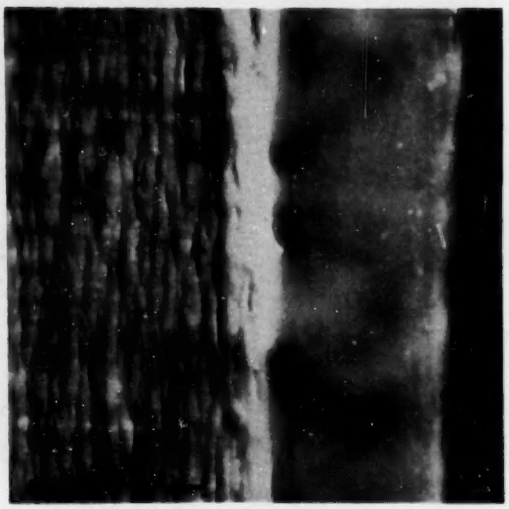

Fig. 22. Ultrathin longitudinal section of Orlon acrylic fiber showing skin-core.

structure was reduced in magnitude but never quite removed completely by using a much harder embedding material. Despite this artifact, we have been able to show a number of interesting structures in fibers made in various ways from acrylonitrile polymers. For example, Figure 22 is a section of an experimental fiber that clearly shows a definite difference between skin and core. In Figure 23, while the polyacrylonitrile shows characteristic chatter marks, the nature of the dispersion of the second polymer in the fiber is clearly recognized. The dark spots are regions where due to poor adhesion between the polymers, the added polymer was lost during sectioning. Figure 24 shows an unusual filmlike fibrillar structure found in an experimental fiber drawn about 20×. Fine cracks have also been found in some polyacrylonitrile fibers, but the compression artifacts made it hard to identify

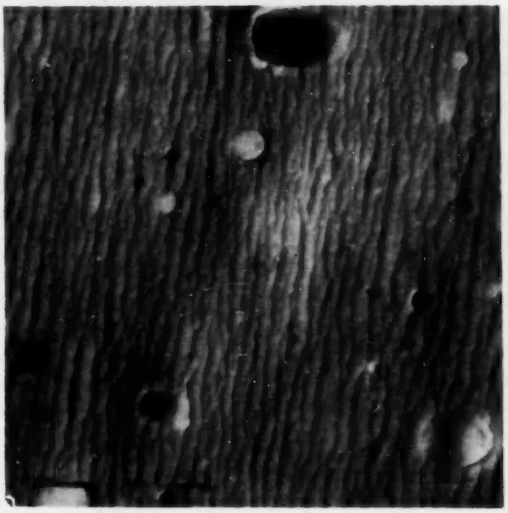

Fig. 23. Ultrathin longitudinal section of a fiber made from a polymer mixture (polyacrylonitrile, the principal portion of the fiber).

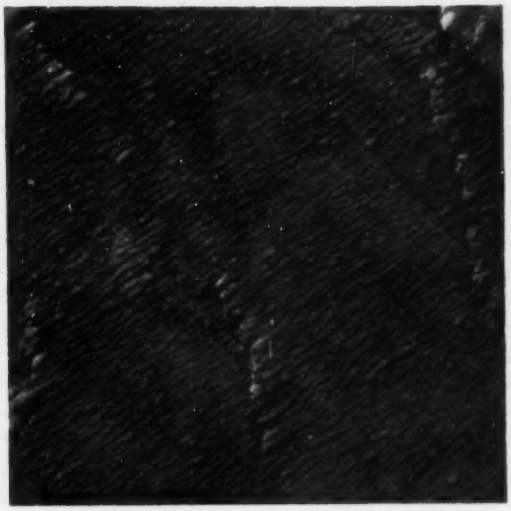

Fig. 25. Ultrathin longitudinal section of experimental Orlon acrylic fiber showing presence of cracks.

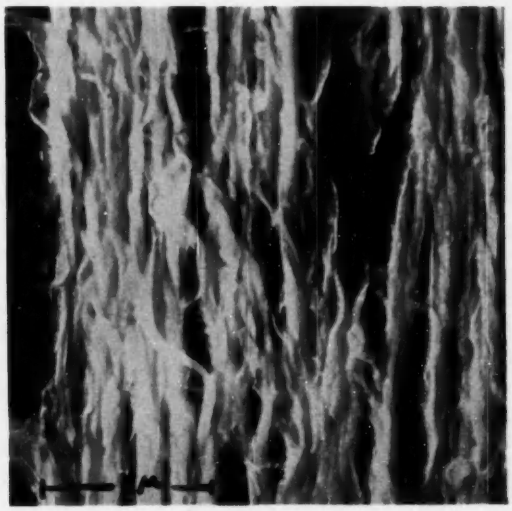

Fig. 24. Ultrathin longitudinal section of experimental Orlon acrylic fiber drawn 20×.

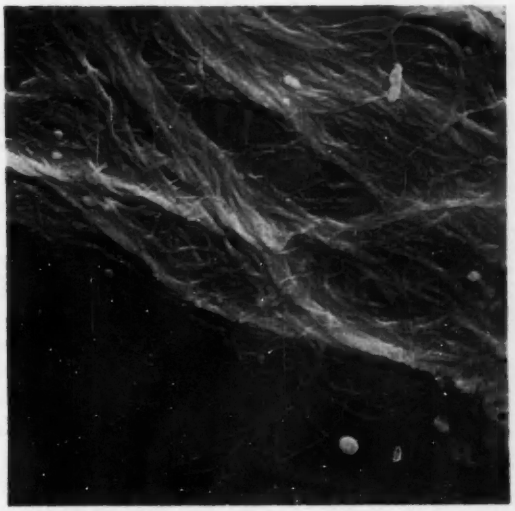

Fig. 26. Longitudinal chemical section of Orlon acrylic fiber (shown in Figure 25) chromium-shadowed before solvent treatment.

them, as seen in Figure 25. We solved this problem in the case of the polyacrylonitrile fibers by cutting the fiber in half along its long axis and making a chemical surface section from the freshly prepared surface. Figure 26 shows the result of this work. The split fiber was surface-insolubilized, and the resulting chemical section was shadowed after treatment with the solvent. The reagent penetrated and affected the entire region of the cracks, rendering their wall insoluble. These show up as sharp ridges in the section. When the chromium shadowing was done before dissolving the fiber away (Figure 27), it was much harder to observe these cracks.

As for polymer structures themselves, we have succeeded in showing a fine granularity in most samples sectioned, particularly in cellulose acetate. This is in agreement with the results obtained by Peck who etched the surface of cellulose acetate fibers with cold acetone and replicated the resulting preparation. No attempt has yet been made to correlate this graininess with polymer molecular size. A few drawn samples of viscose rayon (Figure 20) and cellulose acetate (Figure 28) have been sectioned to show fine randomly dispersed fibrillar structures in the interior of the fiber. Care must be taken in calling these structures characteristic of the fiber since structures similar to these seem to have been produced at the time of sectioning. These latter fibrils are considered artifacts since they occur oriented to the direction of travel of the knife and are always associated with some other distortion.

Pigmented fiber made very good specimens for sectioning procedures. In this case, since the particles are dispersed throughout the section, shadowing is unnecessary, and if the particles are small, such enhancement of surface structures may interfere with the definition of the particles. The sectioning of pigmented fibers is illustrated in Figures 29 and 30. Mechanically cut sections of this sort are limited to dispersed particles having diameters of less than the thickness of the section. Larger particles will be torn from the section at the time of cutting, as shown in Figure 29. However, if solvent sectioning is used, particles of any size in any portion of the affected volume will be carried along with the section as shown in the surface section of pigmented cellulose acetate (Figure 11).

Though the technique of cutting thin sections for use in light microscopy was practiced for many years before the advent of the electron microscope, fundamental principles involved were not well understood and it has only been within the past five years that cutting sections of 0.1 μ or less could be considered a routine procedure in biological studies. The main problem that has retarded extending these techniques to the study of textile fibers was that of the requirements of specimen embedding necessary for the production of such sections. The mounting medium had to have a hardness equal to or greater than that of the fiber being sectioned. This medium should have little or no physical effect on the fiber, yet when cut into ultrathin sections, the sectioned

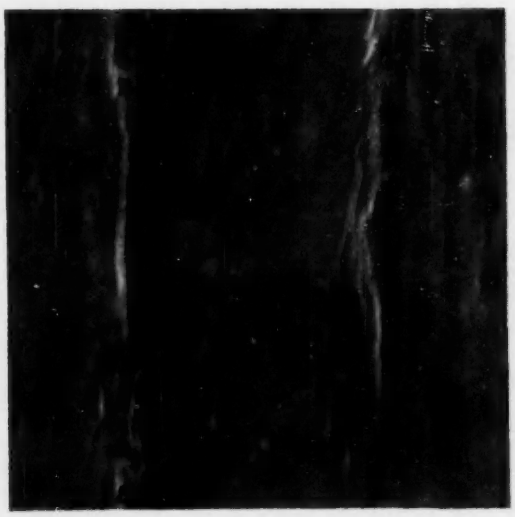

Fig. 27. Longitudinal chemical section of Orlon acrylic fiber (shown in Figure 25) chromium-shadowed after solvent treatment.

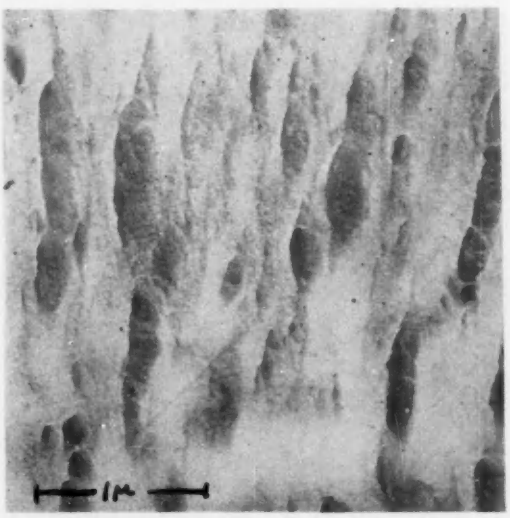

Fig. 28. Ultrathin longitudinal section of experimental cellulose acetate fiber.

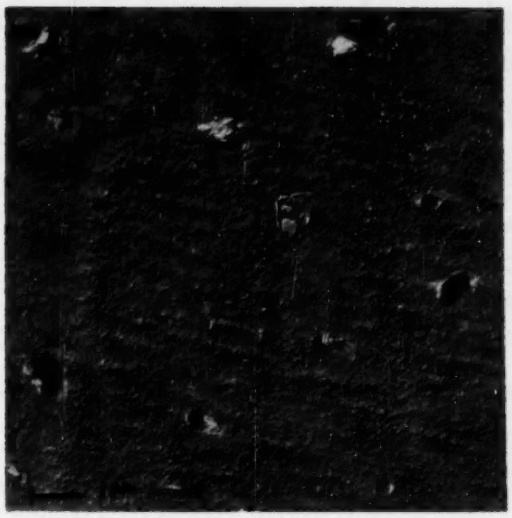

Fig. 29. Ultrathin cross section of pigmented cellulose acetate showing voids produced by tearing out large particles during sectioning.

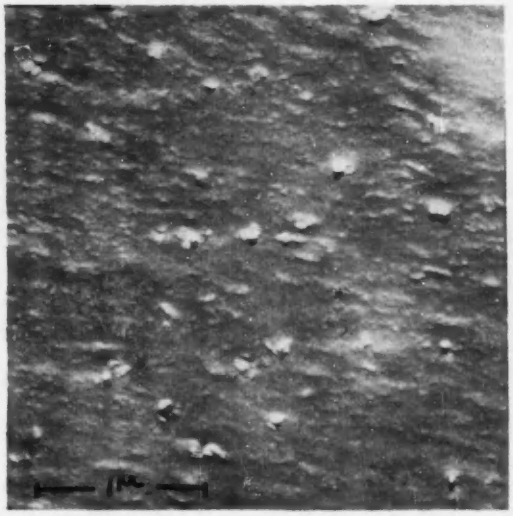

Fig. 30. Ultrathin cross section of pigmented cellulose acetate.

embedding material should retain a hold on its companion fiber section. If the adhesion is insufficient, the fiber section will fold, tear, or be lost in the process. A few fibers such as cellulose acetate and nylon have been sectioned using standard embedding techniques.

The embedding medium used in work reported here consisted of 90% styrene, 9.7% Primol-D [4] and 0.3% benzoyl peroxide. The sections were cut using a Servall microtome with a mechanical advance and freshly prepared glass knives. After the sections were picked up on Formvar-coated screens, they were washed with carbon tetrachloride to remove the embedding material. It was found, as reported by others, that chromium shadowing after such a treatment aided in resolving structural detail on the surface of the sections. In sectioning other fibers, however, we found it necessary to evaporate a thin coat of silica onto the fiber surface before embedding it in a suitable polymer. We thereby increased the adhesive forces between the fiber and the embedding material. With this technique we have been able to section all of the synthetic fibers including Teflon [5] tetrafluoroethylene fiber.

Electron microscopy of synthetic fibers, though still in a formative state, has been shown to be useful in giving a clearer picture of the fibers than was previously possible. Information concerning the effects of chemical and physical agents on fiber surfaces and structural alterations produced by additives is now readily available. Work is now in progress to apply the instrument in a more careful study of structural differences in the polymer that go to make up the fiber.

It must be remembered, however, that when one goes to the high magnifications possible in electron microscopy, one automatically restricts the area of the sample that can be conveniently studied and micrographed. This poses problems of obtaining a representative sample. This can be expedited by proper use of a light microscope and illustrates the interdependence of these instruments.

Conclusions

Techniques for the preparation of fiber sections sufficiently thin for electron microscopy have been developed. Sections may be prepared by microtoming provided that adequate adhesion to the embedding medium is obtained. This has been realized for a wide variety of fibers by coating them with a thin layer of evaporated silica. Sections may also be prepared to advantage by insolubilizing a thin layer of the surface to be examined, followed by solvent removal of the remainder of the sample. The surfaces examined may be the original surfaces of the fibers which yield surface sections and thereby furnish directly the same type of information conventionally sought by surface replication techniques.

[4] Standard Oil Company (New Jersey) trademark.
[5] Du Pont trademark.

The method can also be applied to surfaces generated from the interior of the fiber samples by cutting, fracturing, tearing, etc., and frequently offers advantages over mechanically cut sections.

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The Effect of Cotton Fiber Strength on the Properties of 2-Ply Carded Yarns

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Abstract

Two cottons (Hopi Acala 50—an irrigated variety, and Variety A) and the single yarns used in a previous study, plus yarns spun from an additional cotton, identified as Variety B, form the basis for the 2-ply constructions covered by this report. The single yarns were spun (Z twist) using twist multipliers ranging from 2.75 to 5.75 in increments of 1.00. Each single yarn twist construction was 2-ply twisted (S twist) with the same range of twist multipliers. In addition, a "balanced" ply twist construction was made wherein the ply twist multiplier was found to be approximately 0.7 times the single yarn twist multiplier. Single yarn number was held as constant as possible by varying the spinning draft to compensate for the contraction due to twist.

It was found that for cottons of comparable fiber length and weight fineness, the stronger fibered cotton produced the stronger 2-ply yarns. Also, differences in fiber strength do not affect twist-strength trends or percentage gain in strength of 2-ply over single yarns. The results of this study also indicate that fiber elongation is directly related to 2-ply yarn elongation.

Introduction

Recently the authors reported [6] on the effect of cotton fiber strength on single yarn properties and on processing behavior of two cottons comparable in length, fineness, and maturity, but differing in strength. This report covers the effect of cotton fiber strength on the strength and elongation of a series of 2-ply yarns of varying twists and shows to some extent how single yarn properties are related to the properties of 2-ply yarns. Yarns for this study were prepared from the same two varieties of

[1] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, United States Department of Agriculture.

cotton, and in addition, from a third variety comparable in length and weight fineness but differing in maturity and strength.

Since the twisting of cotton yarns into 2-ply construction is a basic operation in the manufacture of many textile products and since strength is an important criterion of quality in many instances, it would be highly desirable to know the relation of fiber strength to ply yarn strength. Furthermore, the development of new high strength cotton varieties, one of which is being grown on a small commercial scale, makes it desirable that information on the contribution that fiber strength makes toward ply yarn properties be obtained as a necessary step to determine whether or not the expansion of these varieties on a commercial basis is justified.

Berkley and Barker [2] reported "that a significant correlation exists between X-ray angle and the percentage increase in skein strength of a 36/2 yarn over twice the skein strength of the 36/1." Generally, X-ray angle and fiber strength are considered to be closely correlated [3]. More recently, Johnson and Kerr [10] showed that a high strength cotton, when compared with controls of lesser fiber strength, made stronger ply yarns, averaging about 121% of the strength of the controls. However, they found that some of the fiber and single yarn strength does not carry over into these advanced constructions. In addition, Webb and Richardson [14] in a statistical study using a series of single yarn numbers from 22/1 to 60/1 concluded that fiber strength is less important than fineness in cottons 7/8 to 31/32 in. in length, but more important for cottons 1 to 1 3/32-in. in length.

Procedures and Methods

Two cottons (Hopi Acala 50—an irrigated variety, and Variety A) and the single yarns (22/1 and 50/1) used in the previous study [6], plus the yarns spun from an additional cotton, identified as Variety B, form the basis for the 2-ply constructions covered by this report. The fiber properties of these cottons are shown in Table I, with photomicrographs being shown in Figure 1. It is of interest that the higher fiber strength values appear to be associated with the specimen showing the greatest uniformity of fiber shape and cell wall development in the photomicrographs.

Data on 12/1 and 36/1 yarn numbers which were included in the study are not being reported since the characteristics of the 22/1 and 50/1 yarns reflect fully the trends established by the range of yarn numbers processed. The single yarns were spun (Z twist) using twist multipliers ranging from 2.75 to 5.75 in increments of 1.00. Each single yarn twist construction was 2-ply twisted (S twist) on a Whitin [2] twister (4½-in. gauge) with the same range of twist multipliers. In addition, a balanced ply twist construction was made wherein the ply twist multiplier was found to be approximately 0.7 times the single yarn twist multiplier. The balanced characteristic of this ply yarn was determined immediately after twisting by taking the yarn off the side of the bobbin and then observing whether or not a loop of yarn folded or twisted on itself. It is recognized that the balanced characteristic of a yarn is dependent on local processing conditions and on the twist constructions used to produce it, and that

TABLE I. Summary of Fiber Properties

Fiber property	Hopi Acala 50	Variety A	Variety B
Grade			
Classer	SLM+	SLM+	M+
Length			
Classer, in.	1-3/32	1-3/32	1-1/8
Suter-Webb			
UQ, in.	1.24	1.23	1.32
Mean, in.	1.06	1.01	1.11
C.V., %	26	31	28
Fibrograph			
UHM, in.	1.11	1.06	1.18
Mean, in.	0.91	0.83	0.95
UR, %	82	79	81
Fineness			
Suter-Webb, μg./in.	3.90	4.10	3.90
Micronaire	4.60	4.50	3.70
Arealometer			
Specific area, mm.²/mm.³	427	424	469
Perimeter, μ	46.45	46.21	54.70
Cell wall thickness, μ	2.92	2.95	2.49
Weight fineness, μg./in.	4.21	4.21	4.52
Immaturity ratio	1.58	1.56	2.04
Maturity			
Sodium hydroxide method, %	93	90	75
Strength			
Pressley Index, lb./mg.	9.20	7.60	6.20
Stelometer, g./grex			
0 mm.	4.45	3.94	3.42
2.5 mm.	2.24	1.94	1.92
Elongation			
Stelometer, % at 2.5 mm.	8.0	9.0	10.7
X-ray angle			
(degrees at 40% intensity)	30.10	33.20	35.40
Wax content, %	0.57	0.73	0.79

[2] The mention of trade products does not imply their endorsement by the Department of Agriculture over similar products not mentioned.

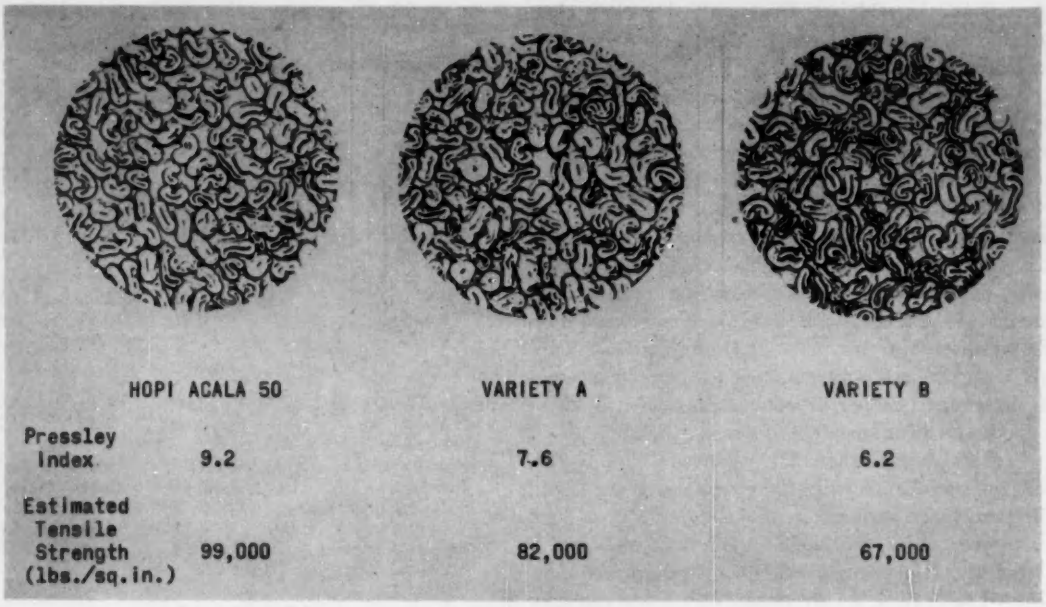

Fig. 1. Photomicrographs of three cottons differing in fiber strength.

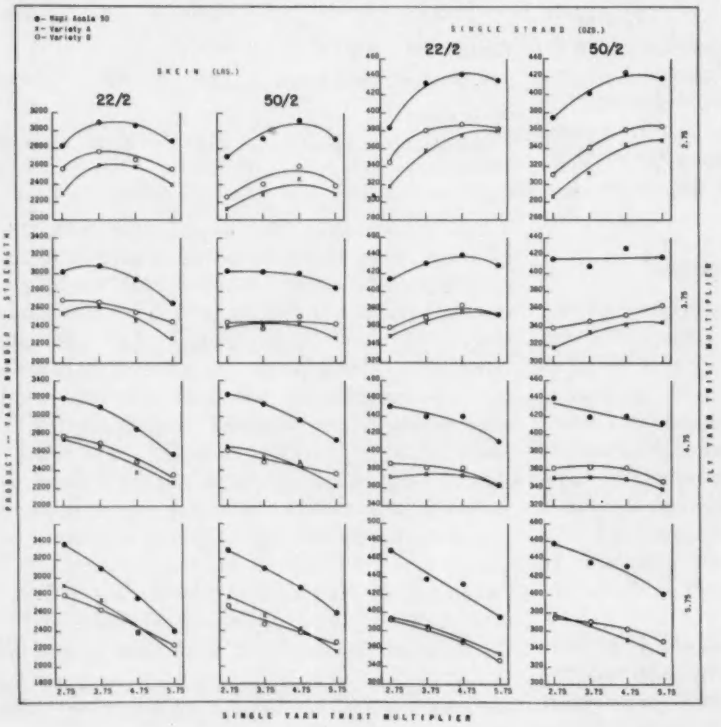

Fig. 2. Effect of single yarn twist on skein and single strand count-strength product of 2-ply carded cotton yarns.

it is subject to small adjustments. Single yarn number was held as constant as possible by varying the spinning draft to compensate for the contraction due to twist.

All tests and test conditions were in accordance with A.S.T.M. procedure [1], except for the Stelometer [13], X-ray angle [12], and wax-content determinations [5]. Skein strength determinations were made on a pendulum-type tester; single strand strength and elongation, on an IP-2* inclined-plane-type tester.

Analysis of Data

The effect of fiber strength on the strength and elongation of 2-ply yarns was analyzed from three standpoints: (*1*) Varying single yarn twist while holding ply yarn twist constant; (*2*) balanced and equivalent (same twist multiplier used for both single and ply yarn) ply twist; and (*3*) ply to single yarn count-strength product ratios.

Effect of Single Yarn Twist

Strength Data

Figure 2 shows curves which relate single yarn twist to skein and single strand count-strength product when the twist multiplier in the ply yarn is held constant. The patterns of these twist-strength curves are generally similar for the three cottons, for both yarn numbers and all ply twist multipliers. Also, the single yarn twist multiplier required for maximum strength is about the same for each of the three cottons, for both yarn numbers, and for most of the ply twist multipliers. These curves are somewhat parabolic for the 2.75 and 3.75 ply twist multiplier, approach linearity for the 4.75 twist multiplier, and are generally linear for the 5.75 twist multiplier for both yarn numbers and method of test. As a result, there is a maximum strength plateau for ply yarns of low twist (2.75 T.M.) but only one point of maximum strength for ply yarns of high twist (5.75 T.M.), since in this area, single yarn twist and strength are inversely related. Another observation is that the single yarn twist required to obtain maximum strength increases with increases in yarn number for the low ply twist yarns (2.75 and 3.75 T.M.). It is interesting to note that the variety having the strongest fiber not only produced the strongest yarns but also responded similarly to twist, as did the control cottons.

These single-ply, twist-strength relationships agree, in general, with the findings of other studies [4, 6 through 9].

Elongation Data

Figure 3 shows curves which relate single yarn twist to elongation at break, when twist in the ply yarn is held constant. Generally, regardless of cotton, yarn number, or ply twist multiplier (except for the 5.75), increases in single yarn twist multipliers produce increases in elongation. However, as the ply yarn twist multipliers and yarn numbers increase, the effect of single yarn twist on elongation becomes progressively less. Of particular interest is the fact that the cotton having the highest fiber elongation (see Table I) generally produced single [3] and 2-ply yarns with the highest elongation.

This relationship of fiber elongation to yarn elongation may provide a basis for emphasizing the probable importance of this fiber property as a contributor to yarn and fabric quality and to processing efficiency. The increasing attention being given elongation as an important fiber property is due as much to the development of precision instruments for its measurements as to the increased appreciation of its probable influence on yarn and fabric quality.

Effect of Balanced and Equivalent Twist

Strength and Elongation Data

Figures 4 and 5 show curves which relate single yarn twist to skein and single strand count-strength

[3] Unpublished data obtained during study previously reported [6].

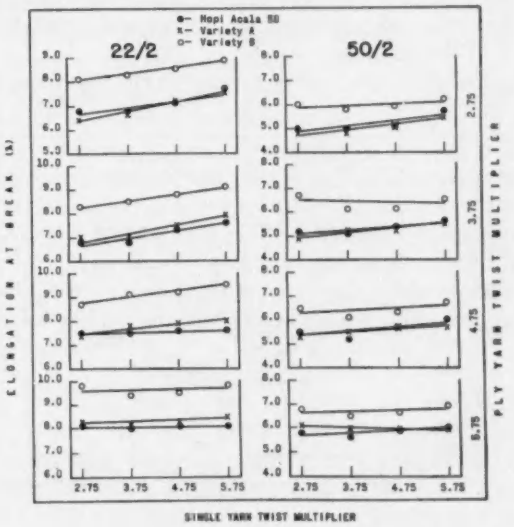

Fig. 3. Effect of single yarn twist on single strand elongation of 2-ply carded cotton yarns.

product when the twist in the ply yarns is balanced and when based on equivalent single and ply yarn twist multipliers. These twist-strength curves, like those presented previously, are very similar in character for the three cottons being studied. Generally, for both methods of test the equivalent twist multiplier required for maximum strength becomes somewhat greater with increasing yarn number. Also, with a few exceptions, yarns made with equivalent twist constructions reach maximum strength at lower twists than those made from balanced twist multiplier constructions. This shift in twist causes the balanced yarns to be generally stronger than those made from equivalent twist multiplier constructions when the single yarn twist multipliers used as a basis are in the range from the point of maximum strength and above. In contrast, with lower single yarn twist multipliers, the former yarns are generally weaker than the latter. Even with the so-called balanced and equivalent ply twist constructions, over a practical range of twists the variety having the strongest fiber produced the strongest 2-ply yarns.

One basic difference between the data obtained from skein and single strand methods of test is that maximum strength values for either the equivalent or balanced twist constructions are obtained with lower twist constructions for skein than for single strand over the range of yarn numbers studied. This difference in twist multiplier required to produce maximum skein and single strand strength applies not only to 2-ply constructions, but also to single yarns, which has been observed by Mercier and Schoffstall [11] among others.

Figure 5 also shows curves which relate single yarn twist to single strand elongation when twist in the ply is balanced and when based on equivalent single and ply twist multipliers. Yarns produced by either twist construction are of about equal elongation. This conclusion was not surprising since the difference in ply twist between the balanced and equivalent twist multiplier constructions is so small for the same basic single yarn twist multiplier that the effects on the elongation characteristics of ply yarns are negligible.

Ply to Single Yarn, Count-Strength Product Ratios

To determine the gain in strength of ply over single yarns made from the three cottons, ply to single yarn count-strength product ratios were calculated for various combinations of single and ply twist multipliers.

Figure 6 shows these count-strength product ratios based on 2-ply skein and single strand strength values.

The per cent gain in strength of ply over single yarns shows the same general trend for both skein and single strand values. Generally, these ratios begin at a peak with low single yarn twist, drop to a minimum with medium single yarn twist, then increase with increasing single yarn twist. For the

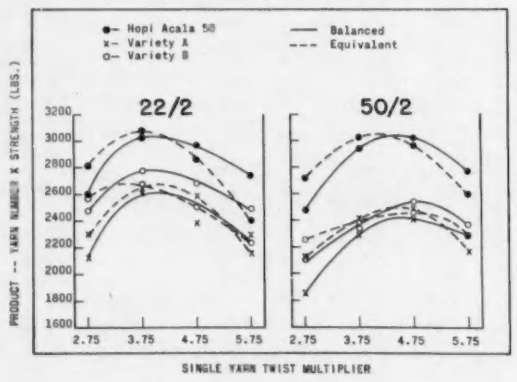

Fig. 4. Effect of "balanced" and equivalent ply twist on skein count-strength product of 2-ply carded cotton yarns.

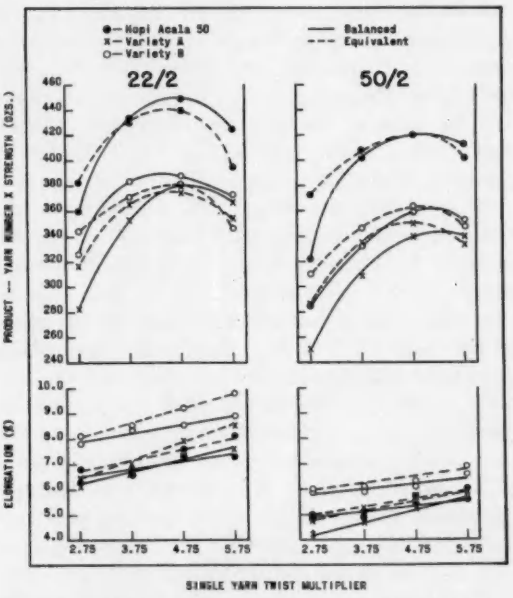

Fig. 5. Effect of "balanced" and equivalent ply twist on single strand count-strength product and elongation of 2-ply carded cotton yarns.

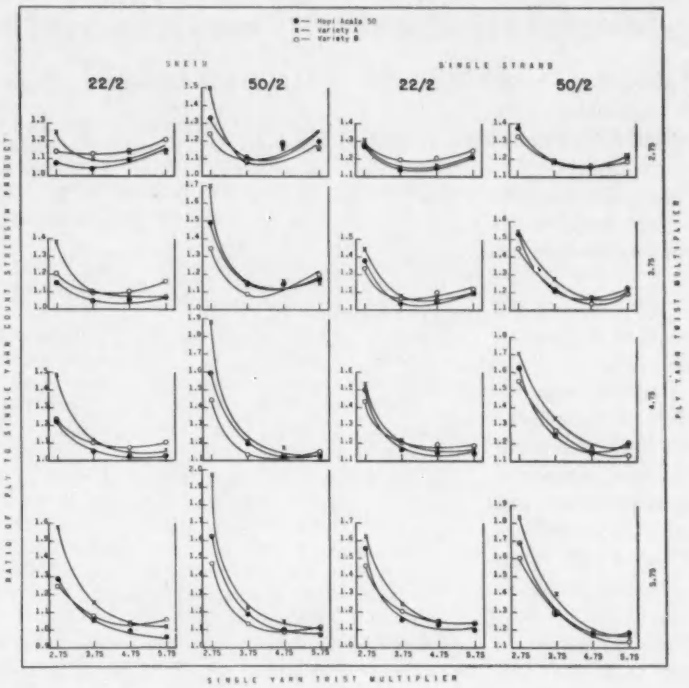

Fig. 6. Ratio of ply to single yarn count-strength product.

relatively low single yarn twist multipliers, the ratios increase with increases in ply yarn twist and with increases in yarn number. The maximum ratios are 1.57 and 1.97 for 22/2 and 50/2 skein values, respectively; and 1.62 and 1.83 for comparable single strand values. They occur in yarns produced from Variety A, the medium strength variety in the series. These results confirm those reported in studies [7, 8] of the effect of single and ply yarn twists on ply yarn properties in which it was shown that low twist single yarns gained more strength-wise than medium or high twist single yarns when 2-ply twisted, with the maximum ply to single strength ratio resulting from the low single twist–high ply twist construction.

Generally, the ratios are positively correlated with ply twist when low twist (2.75 T.M.) single yarns are used, change little when medium twist (3.75 T.M.) single yarns are used, and are inversely correlated with ply twist when high twist (4.75 and 5.75 T.M.) single yarns are used.

The gain in strength of 2-ply yarns over single yarns is approximately the same for these three cottons, regardless of fiber strength or X-ray angle. However, an interesting exception occurs in the case of 2-ply yarns produced from low twist (2.75 T.M.) single yarns. Since Variety A produced, in most cases, the outstanding exception with this construction, it is probable that some factor other than fiber strength or macrostructure (twist and yarn number) contributes to the strength advantage gained by this variety in this particular 2-ply construction.

It is concluded that when fiber strength is the major contributing property in a cotton (fiber fineness and length being about equal), the gain in count-strength product of ply over single yarns is independent of differences in fiber strength since the strongest fiber did not exhibit the largest gain of ply over single yarn count-strength product. It is probable that some fiber property other than strength influences this ply yarn property.

Conclusions

Within the experimental conditions of this investigation, it may be concluded that for cottons of comparable fiber length and weight fineness

1. Fiber strength differences carry over into 2-ply yarns regardless of twist constructions or yarn numbers.

2. Fiber strength does not influence the characteristics of the twist-strength relationship of 2-ply yarns.

3. Fiber strength does not influence the twist multiplier required to produce maximum yarn strength when 2-ply yarns are produced with equivalent single and ply yarn twist multipliers. Incidentally, the single yarn twist multiplier required for this maximum strength 2-ply yarn construction is the one required to obtain maximum strength for the component single yarn.

4. Fiber strength differences do not influence ply to single yarn strength ratios, except in the case of low single yarn twist.

5. Generally, ply yarns gain strength with increases in ply twist multipliers when the component single yarns are of low twist, change little in strength with increases in ply twist multipliers when the component single yarns are of medium twist, and lose strength with increases in ply twist multipliers when the component single yarns are of high twist. This conclusion is independent of the fiber strengths and yarn numbers used in this study.

6. The study indicates that fiber elongation is directly related to 2-ply yarn elongation.

Since fiber strength is directly related to 2-ply yarn strength and does not affect twist-strength trends or percentage gain in strength of 2-ply over single yarns, high strength cottons should find ready acceptance in the production of 2-ply yarns, particularly where strength is an important end-use requirement.

Acknowledgment

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A Comparison of Gradient and Flotation Methods for Determining Density of Degraded Cotton

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Abstract

Using specific gravity columns, the densities of a series of laundered cotton fabrics at 13 levels of regain were determined and compared with values obtained by a flotation method. Pretreatment to remove entrapped air included either centrifuging in organic liquids or boiling in xylene. Water sorption and density curves of the laundered cottons were compared with those of an unlaundered control. Stamm's formula was used for calculations of apparent compression of water.

With the unlaundered cotton at low levels of regain, where presumably no mechanically held water is present, all methods gave comparable results. Variation in values appeared in the control above 3% regain and in the cottons degraded by laundering at all humidity levels. Boiling laundered samples in xylene caused a significant rise in density value.

A statistical analysis showed that the gradient method is less sensitive and less reliable than the flotation method for density determinations on degraded cottons.

Introduction

Determinations of densities of cotton fibers are tedious and involved. This work was undertaken to evaluate the sensitivity of simpler, newer techniques using a density gradient tube on a series of degraded cottons over a wide variation of moisture regain. For this purpose, a series of laundered cottons which had been studied previously [11, 12] for degradative effects shown by tensile strength loss, cuprammonium fluidity increase, and visual damage effects using the Congo red staining technique, were conditioned to 13 levels of relative humidity. The experiment was planned so that information on sorptive ability and density changes of the degraded cotton might be obtained simultaneously with the study of variability in density methods.

Density determinations by the flotation method of Abbott and Goodings [1] were used as a standard at each relative humidity level chosen. Against this, newer techniques using a density gradient column were developed and checked. The results obtained were compared statistically.

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Experimental Methods

The cotton used was high-grade unsized tarantulle, 36 in. wide, having 100 picks and ends per inch and weighing 3.8 oz./sq.yd. Samples had been subjected to a standardized domestic laundering procedure using a gyrator washing machine with wringer and had been dried outside on the roof exposed to June sunshine [9]. Samples at 0, 50, and 100 washing levels were chosen for the study.

Conditioning and Moisture Regain Determinations

A method of conditioning and determining moisture regain of fibers based on that employed by Abbott and Goodings [1] was used. Unless otherwise noted, all tests were made on loose fibers teased out from the yarns unravelled from laundered or unlaundered fabrics as the case may be. From each sample, approximately 0.75 g. of unravelled material was suspended in a weighing bottle by means of a fine acid-resisting wire with a loop at the upper end. A glass tube was inserted into the one-hole rubber stopper used to fit the weighing bottle, and the wire was placed through the tube, thus suspending the fibers in the atmosphere. A small glass cap was fitted over the top of the opening so that the system was closed to the outside atmosphere. To protect the bundle of fibers from accidental contact with the solution, a platform of woven Fiberglas

was suspended between the solution and fibers. The apparatus is shown in Figure I.

The dry weight was initially determined after suspending the fibers over anhydrous magnesium perchlorate in the weighing bottles which were placed in a tightly sealed desiccator containing the same drying agent. Although this does not represent a bone-dry weight, it is one which is easily reproducible without injury to the fibers.

For the conditioned weight determinations, a series of saturated salt solutions giving increasing relative humidities were substituted in turn in the weighing bottles [2]. In each case extra crystals were added to ensure continued saturation of the solution, and therefore constant relative humidity. Each weighing bottle was placed in a larger airtight jar, which had been lined with felt to delay temperature changes during manipulation. The jars were suspended by strong wire in a water bath operating at 73.0° F. ± 0.05. When sufficient time had elapsed for conditioning, the bundles of fibers were weighed by placing the loop on the upper end of the supporting wire over the hook on the balance. The weighing bottle was allowed to rest on a platform which bridged the balance pan. When weighings on consecutive days differed by not more than 0.0002 g., the fibers were considered to have reached constant weight. This required four to five days except in the initial drying period, which was allowed to continue for three weeks.

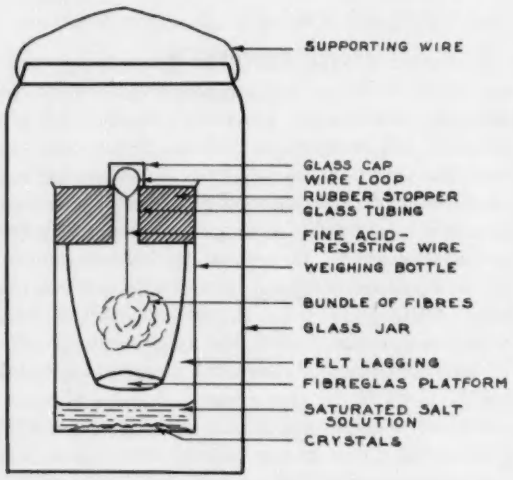

Fig. 1. Apparatus used for conditioning fibers in the moisture regain determinations.

Density Determinations

Due to the porosity of the cotton fiber, the results of density determinations depend upon the medium used [6, 8]. The lumen and smaller capillaries of biological origin and function are thought to be in open communication with the outer world. Evidence to show that organic liquids easily penetrate into the lumen and pore system but not into the substance of the cell wall proper is given by Hermans [6]. Organic liquids are at present considered to give a true rather than an apparent density. This investigation is concerned with the density of the cottons so measured.

Determinations were made on conditioned cottons using (*a*) a flotation method, after centrifuging, and (*b*) a density-gradient method, after either boiling or centrifuging the samples.

(*a*) *Standard flotation method.* After removing entrapped air by centrifuging the fibers in a mixture of organic liquids, the medium is adjusted until the fibers suspend themselves halfway in the tube, at which time they are considered to have the same density as the medium. Details of the operation were as follows:

Fibers were brought to the various humidity levels in the weighing bottles as before. At each level, a few fibers were removed and suspended in the mouth of a small culture tube by means of a fine wire fastened across the mouth with cellulose tape. The tubes were placed in weighing bottles containing the appropriate salt solution, and conditioned in felt-lined containers in the constant temperature-controlled water bath as before. Conditioning was allowed to continue for the same length of time previously found to be adequate for the larger mass of fibers. When conditioning was complete, the bottle was removed, and a mixture of xylene and perchloroethylene of approximately the correct density was quickly poured over the fibers, forcing them into the tubes. The contents of the tube were placed in a 50-ml. centrifuge tube and more of the same liquid added to make the tube two-thirds full. Centrifuging was carried out for 2 min. at 2000 r.p.m., giving a centrifugal acceleration of 900 g. at the tip of the tube. The centrifuge tubes were read at 73° F., the temperature of the bath. Readings were taken at intervals up to 10 min. If the fibers had either risen to the surface or sunk to the bottom, it was concluded that the fibers were lighter or heavier, respectively, than the fluid. A liquid either

lighter or heavier was then added and centrifuging repeated. If the fibers were suspended midway, it was concluded that their density was equal to the density of the immersion mixture, which was then determined pycnometrically.

(*b*) *Density gradient methods* [3, 4, 15, 16]. A density-gradient tube is a vertical column of miscible liquids which have been so mixed that the density changes continuously from top to bottom. Plotting density against height in the column results in a sigmoid curve of which the center third approaches linearity. Fibers dropped into the liquid sink until they reach the level corresponding to their own density.

A density gradient was prepared in a 250-ml. glass-stoppered graduate having 2-ml. divisions. One hundred and twenty-five milliliters of pure perchloroethylene (density 1.62) was added first. The lighter component, which was then poured in carefully down a stirring rod, was a mixture of 60 parts perchloroethylene to 40 parts xylene, giving a resulting density of 1.31. The interface was broken with a thin metal spatula and stirred lightly for 10 sec. The tube was placed in a water bath operating at 73.0° F. ± 0.05, and left for at least 48 hr. before use. Tubes prepared in this way were found to be stable for about three weeks.

The gradient was calibrated by a series of small glass floats of known density. The density of a solution in which the float would just remain suspended at the proper temperature was determined pycnometrically. As a check, the float densities were also determined by a displacement technique, in which the volume of liquid displaced by the floats was determined. Due to the small size of the floats, however, the flotation method was found to give greater accuracy.

Two different methods were used to remove air from the conditioned fibers before placing them into the gradient. In method A, termed the boiling method, the fibers were boiled in xylene for 2 min. and then rapidly transferred to the tube. Method B, the centrifuging method, involved centrifuging the conditioned fibers in xylene for 2 min. at about 900 g. before transfer to the tube. After a 24-hr. period during which the fibers came to stable equilibrium, readings were made to the nearest half division on the graduated tube. Float positions were also read off, the position of the center of volume [1] of each float being taken as the reading for that float's density. By means of daily graphs of density versus position in the tube, the fiber densities were easily determined.

Results

1. Table I shows a comparison of the density values obtained by the three methods. The density-gradient method using centrifuging to remove embedded air gave values closer to those obtained by the Abbott and Goodings flotation method than did

[1] Centers of volume were determined by a displacement technique. After finding the total volume of water displaced, the position on the float was noted when half this volume had been displaced.

TABLE I. Average Density Values Determined by Three Methods on the Series of Laundered Cottons Conditioned to Thirteen Levels of Relative Humidity

Relative humidity (%)	Control			Laundered 50 times			Laundered 100 times		
		Density gradient			Density gradient			Density gradient	
	Flotation method	Boiling	Centrifuging	Flotation method	Boiling	Centrifuging	Flotation method	Boiling	Centrifuging
0	1.538	1.541	1.541	1.441	1.491	1.466	1.387	1.493	1.392
11.1	1.542	1.544	1.545	1.445	1.479	1.463	1.390	1.475	1.395
22.9	1.547	1.548	1.549	1.449	1.491	1.455	1.394	1.499	1.405
32.9	1.541	1.548	1.543	1.438	1.479	1.450	1.402	1.476	1.401
43.9	1.537	1.548	1.544	1.434	1.491	1.459	1.398	1.482	1.411
48.6	1.530	1.549	1.545	1.427	1.495	1.459	1.386	1.487	1.410
53.5	1.529	1.548	1.528	1.422	1.483	1.454	1.378	1.490	1.394
58.5	1.526	1.549	1.542	1.417	1.492	1.451	1.376	1.493	1.399
64.8	1.523	1.548	1.542	1.414	1.492	1.458	1.378	1.491	1.405
75.5	1.511	1.549	1.542	1.425	1.502	1.450	1.388	1.497	1.400
80.1	1.529	1.547	1.536	1.434	1.493	1.457	1.401	1.492	1.400
86.5	1.535	1.546	1.544	1.436	1.493	1.448	1.400	1.478	1.398
92.9	1.530	1.547	1.542	1.433	1.493	1.472	1.399	1.494	1.395

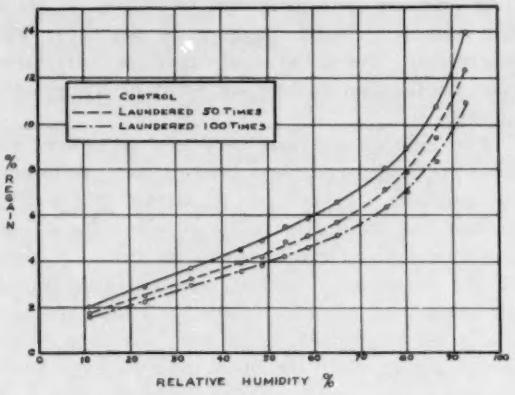

Fig. 2. Moisture regain values plotted versus relative humidity.

the method requiring boiling in xylene as a preliminary treatment. However, the results of the gradient method with centrifuging did not show the consistency of those from the flotation method. In the case of the control, close agreement between all methods was obtained at low regains (below 22.9% relative humidity).

Boiling the unlaundered samples in xylene resulted in a constant density value beyond 22.9% relative humidity conditioning. In both laundered samples, boiling resulted in a rise to roughly the same density at all levels of regain. The density increase noted in the sample laundered 100 times was greater than for the sample laundered 50 times.

2. Water sorption results are illustrated by Figure 2. As the number of launderings increases, sorptive capacity decreases. The middle straight and upper convex portions of the isotherms are evident in all three samples.

3. Density values by the standard flotation method plotted against relative humidity and regain, respectively, are illustrated by Figures 3 and 4. As the number of launderings increases, the density of the cotton samples shows a marked decrease. The density curves reach a maximum about 2.5 to 3.0% regain, decreasing on either side of this value. At high relative humidities, the values show a rise, possibly due to difficulty inherent in the method.

Discussion

Statistical Analysis

A statistical analysis was carried out on the results of all three density methods. The method in which the samples were boiled to remove air showed such deviation in results from the other methods that the variance of interaction between methods and launderings seemed out of line. It therefore seemed advisable to repeat the analysis, using only the results of the gradient after centrifuging, and the standard flotation methods. All levels of relative humidity studied and the three laundering levels were included in this analysis. Table II shows the analysis of variance for these data.

From Table II, it is observed that launderings, relative humidity, and methods all show significant differences. We may conclude that degradation as

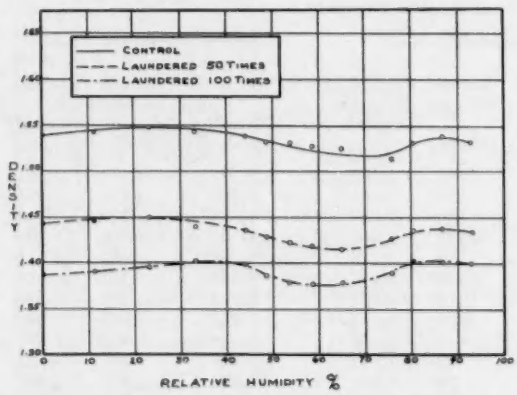

Fig. 3. Density values by flotation method plotted versus relative humidity.

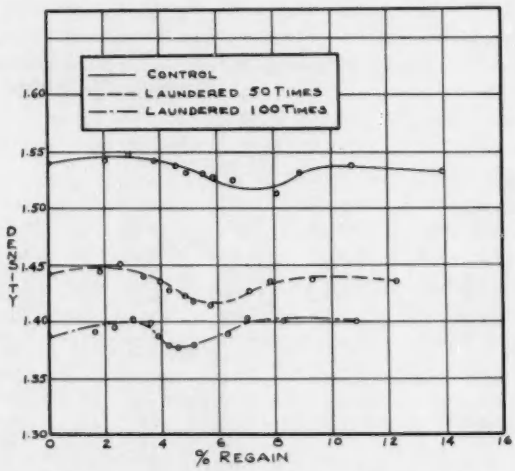

Fig. 4. Density values by flotation method plotted versus regain.

a result of the launderings has caused a significant decrease in density, that relative humidity is a significant factor in these density determinations, and that the two methods analyzed are not interchangeable. It is noted, also, that there are significant interactions between relative humidity and methods, and between methods and launderings, whereas the interaction between relative humidity and launderings is not significant. This indicates that the methods do not correspond with each other at all humidities, and that varying degrees of degradation respond to the methods in a different way.

It is concluded that the methods employed in this study are not interchangeable. The density-gradient method is not sensitive enough for use in a study of cotton degraded to different degrees, and conditioned at various humidity levels.

Methods

The constant density value for the control sample conditioned above R.H. 22.9% obtained by method A would seem to indicate that boiling cotton in xylene removes only the moisture above 3% regain rather than all the moisture. This remaining water must be chemically bound—a view supported by the fact that the density curve reaches a maximum at this area.

The variation in the values obtained by the three methods appears in the control beyond 22.9% relative humidity conditioning and with the laundered or degraded cotton at all conditioning levels. This variation possibly is due to differences in rates of diffusion of the organic liquid into fibers which are holding water mechanically or into fibers characterized by voids due to breakdown. Certainly as degradation increases, structural discontinuities would be expected. The close agreement between all methods found for the control at low levels of regain could be explained then by the lack of interference with diffusion of the organic liquid into the cotton due to either water mechanically held or to degradative effects. For at these low regains, only chemically bound water is present, and in the control, degradation has not occurred appreciably. With only chemically bound water present moreover, air in the fiber pores could be removed more easily.

Boiling both laundered samples in xylene caused an increase in density to a fairly constant value. This may be due to an increase in the proportion of crystalline to amorphous area, resulting from an actual hydrolytic destruction by heat of parts of the amorphous areas which had been sensitized by previous treatment. It is a well-known fact that cellulose partially degraded by oxidation hydrolyzes readily. Density values for both 50- and 100-times-laundered samples are similar after boiling and seem to be independent of regain. This might be expected because of the loss of loosely held moisture during the boiling.

Water Sorption Study

Water sorption curves determined in this investigation follow closely the isotherms described by Hermans [8] and others. The initial sharp rise at very low regains is not shown, because the lowest relative humidity in the series was 11.1%. However, it would be present since the curves must pass through the chosen origin. This initial steep rise has been attributed to that water which enters into chemical combination with the cellulose. The flat

TABLE II. Analysis of Variance of Density Values from Gradient after Centrifuging and Flotation Methods

	Sum of squares	Degrees of freedom	Variance	"F"	5% point
Relative humidity	3686	12	307	5.3	2.18*
Methods	8522	1	8522	147	4.26*
Launderings	536931	2	268465	4629	3.40*
Interaction R.H. × methods	2377	12	198	3.41	2.18*
Interaction Methods × launderings	2037	2	1018	17.55	3.40*
Interaction R.H. × launderings	1924	24	80	1.38	1.98†
Second-order interaction (taken as error)	1400	24	58		

* Significant.
† Not significant.

central portion of the isotherm is thought to be a mechanical filling of small pores and capillaries, while the rapid rise beyond 70% probably represents the filling of larger capillaries.

Laundering causes a progressive decrease in the amount of water sorbed at any relative humidity. Although a lowered water sorption sometimes indicates a decrease in the proportion of amorphous to crystalline material, such an alteration of these fractions is not likely in this case, because of an accompanying decrease in density. Therefore it is assumed that the amorphous region has undergone some change which has lowered its capacity to hold water. Much of the water sorbed by cellulose is held by hydrogen bonds between the oxygen atom of the water molecule, and the hydroxyl of the cellulose chain [17]. A reduction in the number of hydroxyls in the amorphous area could therefore decrease the water-holding capacity. Such an alteration would be found with oxidative degradation, which results in formation of aldehyde, ketone, or carboxyl groups at these centers. Previous studies [9] on this series of cottons had shown an increase in cuprammonium fluidity and a decrease in tensile strength as the number of launderings was increased. These effects are associated with this type of oxidation. Congo red techniques on the series showed that the effect is mainly on the fiber cuticle, the extent of destruction increasing with the number of launderings.

Density

Density curves obtained by the Abbott and Goodings method [1] follow in a general way those obtained by Stamm and Seborg [13], Meridith [10], and Hermans [6], up to fairly high humidities. In the control, there is an initial rise to a maximum value at 22.9% relative humidity, and 2.5 to 3.0% regain. This is followed by a gradual decrease in density, which, it is thought, represents the region where water is filling small pores which results in some swelling. At 80% humidity, there is another rise, which may be due to inherent difficulties in the method of determination. Similar trends were noted in the laundered samples, but the final rise occurred at a lower relative humidity.

The initial rise in density curves was explained by Davidson [5] and Stamm and Seborg [13] as being due to compression of the initial water sorbed by the fibers. From Stamm's calculations, it was concluded that the contraction is the result of appreciable molecular forces which are satisfied by electron displacement and hydrogen bonding, and probably by orientation which permits closer packing.

TABLE III. Apparent Compression of the Water in the Series of Conditioned Laundered Cottons

Relative humidity (%)	Compression of water in c.c./g. of cellulose		
	Control	Laundered 50×	Laundered 100×
11.1	0.009	0.007	0.006
22.9	0.014	0.012	0.010
32.9	0.014	0.009	0.016
43.9	0.015	0.009	0.016
48.6	0.014	0.006	0.010
53.5	0.015	0.005	0.007
58.5	0.015	0.003	0.007
64.8	0.016	0.003	0.009
75.5	0.016	0.013	0.018
80.1	0.027	0.020	0.027
86.5	0.036	0.026	0.030
92.9	0.045	0.033	0.037

Using experimentally determined water sorption and density values, Stamm's formula [14] [2] was applied to determine whether the water here was in a compressed state or was simply filling voids. The results are given in Table III. It is observed that up to 75% relative humidity, the values range between 0.003 and 0.016 for all samples, averaging approximately 0.01 cc./g. of cellulose, in which case the average density of the sorbed water would be 1.01 g./cc. Since such a value may be low enough to be caused by experimental error, it may be stated that very little if any compression of the water exists at low regains. Stamm obtained values of 1.04 to 1.25 by similar calculations and concluded that such values were not too great to be reasonable.

The greater values obtained for compression at higher regains may indicate that there has been insufficient swelling to allow the water to remain in the fiber without being compressed to some extent. Conversely, these values could result from calculations in which the density figures were too great. There is the possibility that at high regains, cen-

[2] Stamm's formula

$$C = \frac{m_1 - m_0}{d_w} - \left(\frac{W_b - (W - m_1)}{d_b} - \frac{m_0}{D} \right)$$

Where C = apparent compression of the water in c.c./g. of cellulose. D = assumed density of the cellulose substance. m_1 = wet weight of cellulose. m_0 = dry weight of cellulose. d_w = density of water. W_b = weight of pycnometer and benzene. W = weight of pycnometer, benzene, and wet cellulose. d_b = density of benzene.

trifuging in the course of the determination may have removed some of the more loosely held water from the fibers, thus causing a density increase. Further study would be required to determine which of the above explanations is valid.

Summary

1. Using specific gravity columns, the densities of a series of laundered cottons at 13 levels of regain were determined and compared with values obtained by a flotation method. Pretreatment to remove entrapped air included either centrifuging in organic liquids or boiling in xylene. The gradient method was less sensitive and less reliable for use on degraded cotton over this range of regains.

2. After conditioning unlaundered cotton at low relative humidity levels, all methods gave comparable results. In the method requiring boiling in xylene, density was found to be independent of the conditioning level over 2.5% regain. It is concluded that when only chemically bound water is present, there is no interference with removal of entrapped air or with diffusion of the liquid into the porous cotton. The three methods are then interchangeable. But when cotton is conditioned to higher regains, water mechanically held causes interference. This is thought to account for the variation in the two methods in which cotton is pretreated by centrifuging.

3. Boiling laundered samples in xylene caused a significant rise in density value. It is postulated that the boiling has caused a breakdown of parts of the amorphous regions which had previously been rendered sensitive by the oxidative degradation known to occur during laundering.

4. The water sorption study revealed that as the number of launderings increases, water sorptive capacity decreases markedly. This is thought to be due to a reduction in the number of available hydroxyls in the amorphous region. The oxidation occurring during laundering has resulted in the formation of aldehyde, ketone, or carboxyl groups at the previously available hydroxyls.

5. Density values obtained by the standard flotation method indicate that as launderings increase, the density of the cotton decreases markedly. The density curves reach a maximum at about 2.5 to 3.0% regain, at which time most of the chemically bound water has been taken on. The gradual decrease above this regain is thought to represent the region where the water is filling small voids, resulting in some swelling. Calculations showed that little if any compression of the water exists at low regains.

Acknowledgment

Acknowledgment is made to Dr. A. C. Goodings of the Ontario Research Foundation who suggested the topic and to Mrs. Margaret Ayer and Miss Jane Karstedt who did preliminary work on the density relations of degraded cotton.

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Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

Iodoform Reaction on Jute Hydrolysate

Technological Research Laboratories
Regent Park, Tollygunge
Calcutta 40, India
January 12, 1956

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

During the course of an investigation of the estimation of acetone in acetone-treated jute by iodoform reaction, it was found that distillates from dilute acid and alkaline hydrolysates of jute responded to this reaction. They were also found to reduce ammoniacal silver nitrate and Fehling solution.

Previously the iodoform reaction reported by Huebner and Sinha [3] in the case of cellulosic materials, silk, wool, rubber, etc., and extended to jute by Chatterjee [2], was performed *in situ*. In this investigation iodoform was isolated in the crystalline state by the alkaline iodine oxidation of the distillate from the alkaline hydrolysate of jute. This reaction was further applied, with positive results, to bleached cotton, jute hemicellulose, jute lignin, and D-glucose.

As regards the nature of the compound or compounds responsible for the above reactions in jute, jute holocellulose, bleached cotton, and glucose, at least one of the compounds was acetol, which was identified by the characteristic blue fluorescence in ultraviolet light of the 3-hydroxyquinaldine it formed with *o*-aminobenzaldehyde, according to the methods described by Baudisch and Deuel [1], and Sattler and Zerban [4].

The mechanism of acetol formation from cellulose could be explained by a cleavage in the middle of the nonreducing end-glucose residue of the cellulose chain and subsequent conversion of the hydroxymethyl group into a methyl group. This view was supported by the observation that the distillate from the alkaline hydrolysate of L-rhamnose, which contains a methyl group at the end, formed the highest amount of acetol and took up the highest quantity of iodine in the iodoform reaction in comparison to D-glucose and D-glucuronolactone. A comparison of different quantities of acetol formed was done as before from the intensity of blue fluorescence in ultraviolet light of 3-hydroxyquinaldine.

In the case of preliminary experiments on the iodoform reaction, ordinary jute, 2 g., air-dry, powdered, and defatted with benzene, was treated with 250 ml. of approximately decinormal sodium hydroxide refluxed for 30 min. in a glycerin bath at 120°–130° C. and filtered. In order to carry out a comparative estimation of iodine taken up during the iodoform reaction, instead of refluxing, mixtures were distilled from a glycerin bath kept at 120°–140° C. until 150 ml. was obtained as distillate within 75 min. The distillate with 5 ml. of decinormal iodine in potassium iodide was treated with approximately decinormal sodium hydroxide to a yellow color, left overnight in a dark place, acidified

TABLE I

Nature of sample	Iodine (g.)
Jute	0.95
Jute lignin	2.3
Jute α-cellulose	0.84
Jute hemicellulose	0.73
Jute holocellulose	0.78
Cotton α-cellulose	0.66
D-glucose	6.0
D-glucuronolactone	6.3
L-rhamnose	9.0

with dilute hydrochloric acid, and titrated with decinormal sodium thiosulphate.

Iodine reacting with the distillate from 100 g. air-dry material is given in Table I.

In the case of jute, the distillate obtained by the alkaline hydrolysis method and left after titration with sodium thiosulphate, was kept overnight in a dark place. Yellow, lustrous crystals, collecting at the bottom, melted above 118° C. to a dark red liquid, and gave the isocyanide reaction and other characteristic properties of iodoform.

The author is grateful to Dr. P. B. Sarkar, Director, for his helpful suggestions.

A. K. Sanyal

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Improved Sampling and Shirley Analyzer Operating Procedure

U.S. Cotton Ginning Research Laboratory
Agricultural Research Service
U.S. Department of Agriculture
Stoneville, Mississippi
November 22, 1955.

To the Editor
Textile Research Journal

Dear Sir:

A project was undertaken at this laboratory in an effort to reduce the standard error in foreign-matter-content results of lint cotton, as determined by the Shirley Analyzer.

Attention was first given to sampling procedure. Normally, a 100-g. sample for testing on the Shirley Analyzer is selected in one or two pulls at random from the mass of material to be tested. This "grab" or regular method was checked against a method by which five random pinches of about 10 g. each are drawn from the top and five from the bottom of the mass of material to make up the 100-g. test sample. Each time the mass was turned 180° to select pinches, the foreign material which had sifted out was placed back on top of the mass.

This pinch method of sampling has been found desirable for obtaining a representative specimen from a large sample for nearly all fiber tests, especially those requiring only a small amount of fiber.

Testing Procedure

In an effort to further reduce the variation or standard error noted in Shirley Analyzer test results, the machine and the procedure for making the test were examined. For no apparent reason the amount of invisible loss [1] varied considerably and appeared to be a major cause of the variation in test results. Trials with several exhaust-valve settings failed to have an appreciable effect on the amount and variation of the invisible loss. The standard feed table as attached to our analyzer is 12 in. in length. When the 100-g. sample is spread at one time on this table, the layer of lint is about 3 in. thick, which results in a rapid rate of feed to the machine. It seemed logical to carry a thinner layer and thus avoid crowding the machine. Therefore only half of the sample was spread on the table at one time. A longer table would, of course, accomplish the same result.

The first test by this method gave an average of 17.5% less invisible loss through the exhaust fan than with the former rate of feeding. This is taken to be an indication that less fibers are broken and discharged by the exhaust fan with a slower rate of feed. Since the primary purpose of the Shirley Analyzer test is to determine the amount of foreign matter in a sample, the new method may be considered more nearly correct from the standpoint of reflecting the true foreign-matter content of the test specimen, because errors introduced by erratic invisible loss figures are reduced. Visual inspection of samples processed by both methods indicates no difference in the amount of foreign matter left in the lint after testing.

New Sampling Method and Test Procedure as Compared with the Regular Sampling Method and Test Procedure

In order to compare the new pinch sampling and test procedure with the regular grab sampling and normal test procedure, a large uniform lot of late-season machine-picked cotton weighing approximately 19 lb. was spread evenly over a 3 × 8-ft. table

[1] Loss through exhaust fan and not collected. Probably broken fiber, dust, and possibly some loss in original moisture content.

TABLE I. Shirley Analyzer Data on a Total of 60 Lint Cotton Samples of 100 g. Each, Using Two Sampling Methods and Two Testing Procedures

	10-pinch sampling method and new testing procedure				Regular sampling method and testing procedure		
Sample	Visible waste (%)	Invisible waste (%)	Total waste (%)	Sample	Visible waste (%)	Invisible waste (%)	Total waste (%)
1	9.74	2.18	11.92	1	10.81	2.19	13.00
2	10.33	1.80	12.13	2	11.57	2.79	14.36
3	9.75	2.02	11.77	3	8.88	2.46	11.34
4	9.81	1.99	11.80	4	9.38	2.05	11.43
5	10.08	1.67	11.75	5	9.90	2.47	12.37
6	10.17	1.87	12.04	6	9.60	2.43	12.03
7	9.72	2.10	11.82	7	9.88	2.57	12.45
8	10.31	1.66	11.97	8	10.42	1.48	11.90
9	9.60	1.78	11.38	9	9.34	2.17	11.51
10	10.00	1.66	11.66	10	10.40	1.77	12.17
11	9.27	1.81	11.08	11	8.51	2.10	10.61
12	9.90	1.52	11.42	12	8.59	1.90	10.49
13	10.17	1.48	11.65	13	9.67	2.33	12.00
14	9.64	1.63	11.27	14	10.28	2.00	12.28
15	10.21	2.02	12.23	15	7.94	1.94	9.88
16	9.68	2.12	11.80	16	9.57	2.25	11.82
17	10.35	1.77	12.12	17	10.24	2.02	12.26
18	10.26	1.60	11.86	18	10.81	1.72	12.53
19	10.65	1.56	12.21	19	11.31	1.87	13.18
20	11.23	1.04	12.27	20	10.39	1.39	11.78
21	10.14	1.46	11.60	21	9.29	2.06	11.35
22	10.83	1.37	12.20	22	11.28	1.37	12.65
23	10.28	1.25	11.53	23	11.40	1.67	13.07
24	10.79	1.52	12.31	24	10.68	1.68	12.36
25	10.88	1.38	12.26	25	8.90	1.85	10.75
26	10.95	1.03	11.98	26	11.16	1.68	12.84
27	11.00	1.35	12.35	27	10.51	1.62	12.13
28	11.00	1.14	12.14	28	10.36	1.67	12.03
29	10.42	1.32	11.74	29	10.40	1.44	11.84
30	10.98	1.28	12.26	30	10.66	1.53	12.19
Av.	10.271	1.613	11.884	Av.	10.071	1.949	12.020

for sampling. A total of 30 pairs of samples were drawn and tested alternately by the two methods.

A comparison of the data shows that the invisible loss is reduced an average of 17.2% by using the new sampling method and testing procedure (Tables I and II). The new method of sampling and feeding the machine on the basis of this test has a standard deviation on total waste of ± 0.335 as compared with ± 0.891 for the regular sampling method and test procedure. These data show that the reliability of the test results is improved by using the new sampling method and testing procedure and is recommended especially when small differences between samples are to be measured. Experience has shown that the increase in time from about 15 min. for the regular procedure to 19 min. with the new procedure is well worth while when maximum accuracy of results is desired.

TABLE II. Analysis of Variance on Results in Table I

Source	Degrees of freedom	Visible waste mean square	Invisible waste mean square	Total waste mean square
Total	59			
Between methods	1	0.6021*	1.6968**	0.2775
Between samples	29	1.0167**	0.2042**	0.5246
Error	29	0.1112	0.0379	0.3811
LSD (5%)		0.1761	0.1028	0.3260
LSD (1%)		0.2373	0.1385	0.4393

* Significant.
** Highly significant.

JACOB V. SHEPHERD

INDUSTRIAL SECTION

Survey of Control Chart Applications in Textile Processing[1]

Norbert Lloyd Enrick

Institute of Textile Technology, Charlottesville, Virginia

An increasing number of mills are using statistical control charts as an aid in their quality control programs. The quality-improving and cost-saving features of such control charts, as discussed in the present report, are based on a detailed survey of the cotton and woolen-worsted systems in more than 50 mills in the United States and Canada.

When controlling quality in the textile mill, it is obviously not practical to test 100% of the products at the different stages of processing, and therefore one is obliged to sample exceedingly small portions of production. Often a decision affecting many thousands of pounds must be made from tests on only a few pinches of cotton or short lengths of sliver, roving, and yarn.

Statistical evaluation of test results is therefore an important aid in making the right decision. Statistical control charts have become the chosen tools in the routine control of the quality of production.

Examples of Typical Control Charts

Four representative examples will illustrate the usefulness of each of the most widely used types of control charts in various processing operations of textile mills:

1. Control Chart for Sample Averages

A typical set of control charts used in controlling average weight of stock in a size-control program, from drawing through spinning, is shown in Figure 1. By plotting sizing test results in the form of averages, any trends toward excessively high or low weights become apparent readily, and correction can follow swiftly.

2. Control Chart for Sample Ranges

In addition to control charts for averages, it may also be desirable to control ranges. Ranges representing the difference between the highest and lowest test result in sampling indicate whether or not variability may be excessive. A good example is seen in Figure 2, taken from a fulling operation on a woolen cloth.

3. Control Chart for Defects per Unit

The chart for warper stops per million yards, in Figure 3, is a typical application of the defects-per-unit type of control chart. The stops represent defects, and the million yards is the unit. Other defects-per-unit types would be ends-down per 1000 spindle hr., neps per card web, and many similar types of measurements in the textile mill.

4. Control Chart for Per Cent Defective

The per cent defective control chart is most frequently applied to end product, such as rags and remnants, seconds, and similar losses in first-quality merchandise. However, it can be applied equally well to control processing performance and machinery efficiency, such as the control chart for per cent idle spindles in Figure 4, obtained from random checks in the spinning department. This particular type of application was first developed by Tippett [10] and subsequently modified by McAllister and Nelson [8].

Mill Applications of Control Charts

From a survey in more than 50 mills, supplemented by literature studies, it was determined that charts have been used successfully when applied to the various mill characteristics described below.

[1] Presented in part before the 9th Annual Convention of the American Society for Quality Control, New York, New York, May 24, 1955.

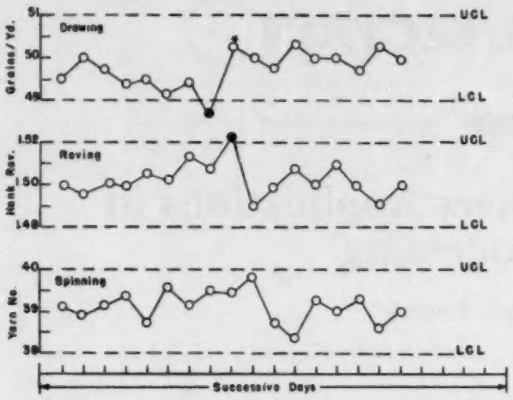

Fig. 1. Control charts for various processing stages. UCL = upper control limit; LCL = lower control limit; circle = test average; shaded circle = outside control limits; * = heavied one tooth on crown gear.

1. Raw Materials Testing

The purpose of these tests is to check the quality of raw stock, to allocate it to the proper production lines best suited for a particular end use, and to blend advantageously compensating quality characteristics. Tests performed for this requirement, supplemented by control charts, are

A. Fiber length, in inches.
B. Length uniformity, in coefficient of variation.
C. Fineness, in micrograms per inch.
D. Pressley strength index.
E. Fiber maturity, in per cent.
F. Microscopic properties, such as Cavitoma [11] and doughnut fibers [1].

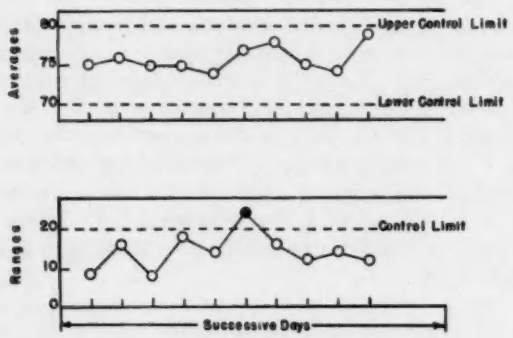

Fig. 2. Control charts for averages and ranges; control of fulling time in minutes. (Out-of-control point, shown by shaded circle, was found to be due to excessive soaping and was subsequently corrected.)

G. Chemical tests, such as for honeydew deposits [9].

H. Fluorescence tests in ultraviolet light, such as for yellow-green spots [10] or so-called "cat-eye" contamination.

Control charts are also maintained on check test samples to ensure that the precision of the test itself conforms to standards.

2. Stock Weight and Variation

Control of these characteristics will result in a yarn that conforms closely to the desired weight with a minimum of deviation and variability. Charts are generally maintained at each processing stage, as shown in Figure 1. One processing department, such as drawing or roving, is generally used as the key control point for making gear changes to keep weights in line [4, 7].

3. Linear Uniformity of Stock

In addition to weight variation, we also need to control the variation in short lengths of a strand of textile material, which occurs due to irregular fiber alignment. The statistical laws of chance state that the maximum variation cannot be better than plus or minus three times the square root of the number of fibers per cross section of yarn. In practice, the actual variation will be higher, due to drafting imperfections [4].

For example, using this formula for a 36's yarn with an average of 100 fibers per cross section, we would find a theoretically expected maximum of

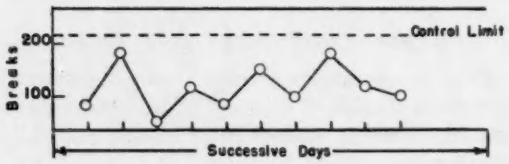

Fig. 3. Control chart for warper stops; control of breaks per million yards. (Where breaks per million yards are checked on a weekly, rather than daily basis, the inscription "successive days" would read "successive weeks," and the actual date of each week should of course be shown.)

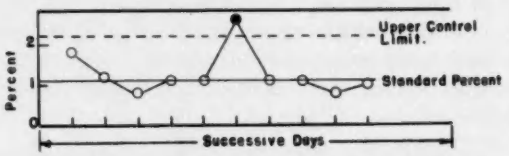

Fig. 4. Control chart for per cent idle spindles.

$\pm 3 \times 10$, or ± 30 fibers per cross section. In actuality, we would normally find a variation one-third to one-half higher, such as ± 40 to 45 fibers per cross section. The degree to which actual variations conform to the theoretical gives us an indication of how well we have been processing the fibers.

In place of maximum variation, we may use the equivalent and related measures of per cent nonuniformity and coefficient of variation, as obtained on such electronic equipment as the ITT-Brush uniformity analyzer with automatic evaluator or the Uster tester.

4. Running Conditions of Stock

Running conditions of stock are evaluated in terms of the rate of ends-down and loom stops. Aside from the fact that a broken strand means lost production until pieced up again, and the piecing-up means additional labor, a high rate of breaks usually indicates nonuniform, weak, and poorly prepared stock. Now in place of ends-down per 1000 spindle hr., some mills prefer to use ends-down per 100 yd. In each case, the expression is known statistically as the "defects-per-unit" type, as discussed above [4].

5. Reworkable and Nonreworkable Waste

Waste in a cotton mill is of either of the two major classifications above and is then broken down further by department and category within that department. Control charts here aid from the standpoint of quality (proper removal of short fibers, trash, and leaf) and cost (keeping avoidable waste to a minimum). Both operator carefulness and proper machine setting may thus be controlled by charting [6].

6. Processing Tests

A large variety of tests may be included under this heading. The first of these is applied to the degree of opening and to feeding percentage, since improperly opened stock fed at a rate other than optimum is already a violation of one of the initial conditions that make for uniform product. Other tests suited for control-chart use are applicable to neps in the card web; to package size of sliver, roving, and yarn; to roll settings; to spoon and trumpet knock-off checks; to roving traverse; to critical speed ratios, such as spindle to front roll for proper twist insertion; and to many others [4].

7. End-Product Evaluation

When the yarn has been spun, it is too late to correct any faults. But, nevertheless, we like to maintain control charts, so as to assure ourselves that the quality remains up to standard. The characteristics for which mills have kept control charts are these:

A. Single-end strength and elongation.
B. Skein strength.
C. Linear uniformity.
D. Defects per 50 yd. of yarn.
E. Appearance grade.
F. Twist, in turns per inch.
G. Twist variation, in coefficient of variation.
H. Moisture content, in per cent.
I. Cloth quality.

Proper control of raw materials and processing conditions during production is the best assurance that the final yarn will meet the end-product specifications.

Discussion

A good measure of the widespread success of quality controls, including control charts, which has been attained in the textile industry, is the continuing reduction of doublings of stock in processing. The mechanical operation of doubling and drafting is equivalent to the statistical operation of averaging and totaling. Consequently, we may call in a proven statistical formula to interpret the theoretically expected effect of doubling and drafting. This formula states that the effect is one of reducing variations by the square root of the number of strands combined. In actuality, due to drafting imperfections, the results predicted by the formula will be accomplished approximately, but not completely [4].

For example, in a cotton mill processing 1 1/16-in. staple, card sliver variation was found to have a coefficient of variation of 5.1%. There were 16 doublings in the subsequent drawing operation. Therefore, by dividing 5.1 by the square root of 16, or 4, we obtain 1.3% as the expected coefficient of variation for drawing sliver. The actual value was 1.5%.

With the aid of statistical quality control, improved testing equipment, and improved design of machinery, textile mills in the past decade have been making less and less variable stock. This in turn has permitted a constant decrease in the number of doublings in processing, at considerable saving in machinery investment and labor costs. Thus, while it

was common not so many years ago to have several stages of doublings on roving frames and spinning frames, many a mill now prides itself on making a good quality yarn without any doublings at all on these processes. Doublings are still required, however, in earlier processing stages and for finer yarns.

Summary

The principal benefit attainable from statistical control charts is their aid in accomplishing the following:

1. More uniform and stronger yarn and cloth attained through proper allocation of stocks, effective control during processing, and periodic testing of final product.
2. Higher production and lower labor costs, due to decrease of ends-down and loom stops.
3. Lower processing costs due to less doublings of stock.
4. Reduced waste due to effective waste controls.
5. Improved salability of the final product because of better quality at lower cost.

The degree to which these benefits are attained depends, of course, on the type of stock processed, the end product, the intensity with which statistical controls are used, and how well the results are observed—from management to the front-line production level.

Often, of course, a mill may feel that quality salvation lies in the purchase of new equipment alone. Yet, it would usually be worth while for such a mill to see first how much can be attained through statistical quality controls. Sometimes this may show that good enough results can be accomplished without necessitating expenditures for as much new equipment as would otherwise be required. The literature on quality control is full of case histories of excessive variations, originally blamed on the equipment, which could be reduced with the aid of control charts. Thus, appropriations for purchases could be saved.

As an example, work in statistical quality control was recently done in a mill in which the slubbers had long been considered unsatisfactory and due for replacement because of excessive variations. Actually, however, statistical analysis showed the high variation found to be due to prior processing. This was corrected readily, and as a result the slubbers automatically produced more uniform roving, so that it is now considered unnecessary to replace them. This represented a considerable saving to the mill.

Acknowledgments

The author wishes to express his appreciation for the helpful comments and suggestions received from Dr. Jack Compton, Technical Director of the Institute of Textile Technology. Special thanks are due John Bevilacqua for drawing the charts in this paper.

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Polyvinyl Alcohol Fibers

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Air Reduction Company, Inc., Murray Hill, N. J.

POLYVINYL alcohol was discovered in 1924 by W. O. Herrmann and W. Haehnel. In 1931 they succeeded in spinning it into fibers. These first fibers were water-soluble and were intended for specialty applications, for which a small market still exists. Serious attempts at insolubilizing the fibers were subsequently undertaken in Germany, England, and the United States.

The Japanese interest in the fiber began in 1935 when they initiated a study of all synthetic fibers. They concluded, as a result of this study, that of all synthetic fibers, polyvinyl alcohol held forth the most promise of being made economically from Japanese raw materials. Accordingly, a polyvinyl alcohol fiber development program was started in 1940 which, with serious setbacks due to the war, culminated in its industrialization in 1949. Thus the history of the polyvinyl alcohol industry is essentially a Japanese story.

The term, vinylon, was adopted as a generic name for polyvinyl alcohol fiber, while the contraction, poval, was applied to polyvinyl alcohol resin. These names will be used throughout this paper.

Early in the project it was recognized that the material could be made in a large number of variations. Since the investigation of any great portion of these variations would seriously increase the time and cost of development, a somewhat arbitrary decision was made to work on the type of vinylon which, to some extent, is represented by the material produced today. This decision is responsible for the early industrialization of vinylon, which in turn is responsible for the rapid improvements in technology, quality, and cost. A detailed study of the first two is a prerequisite to an understanding of the latter.

The basic raw materials for vinylon are coal, limestone, salt, sulfur, air, and electricity. Although there is an abundance of low-quality coal in Japan, high-quality coal must be imported. Salt must also be imported. Hydroelectric power and the other materials are available in Japan. Coal and limestone are converted in the conventional manner into calcium carbide and thence into acetylene. The carbon monoxide from the carbide furnaces goes into methanol and formaldehyde, while sulfur is converted into sulfuric acid and sodium sulfate. Salt finds its way into caustic soda and chlorine, the latter going into vinylon bleaches.

In Figure 1, we have represented an integrated poval plant of the type currently used in Japan. This plant has units for the synthesis of acetic acid from acetylene, the synthesis of vinyl acetate from acetylene and acetic acid, the continuous polymerization of vinyl acetate, the continuous alcoholysis or saponification of polyvinyl acetate to the alcohol, and the recovery and recycling of coproducts. The essential steps in the production of vinylon filament are depicted in Figure 2.

The quality of vinylon is influenced by virtually every step in its production. The degree of polymerization and the uniformity of degree of polymerization influence the strength of the material. The technique of spinning can influence both strength and elasticity. This includes wet or dry spinning, concentration of spinning solution, concentration and composition of spinning bath, and cross-sectional shape of the filaments. Drawing results in molecular orientation in the filament and greatly influences the strength of the fiber. It must be done gradually at first and then more strongly. Some drawing is even accomplished during the formation of the spun yarn. The primary purpose of heat treatment is to improve water resistance. It too must be carefully controlled.

The original objective in acetalizing the fiber was to improve the water resistance. For this purpose, formaldehyde was quite suitable and is still used for the bulk of the commercially produced fiber. If the formaldehyde is introduced after drawing and heat treatment, it does not alter the X-ray diffraction

[1] Manager of the Development Staff, Research and Engineering Department, Air Reduction Company, Inc.

[2] Project Manager, Research and Engineering Department, Air Reduction Company, Inc.

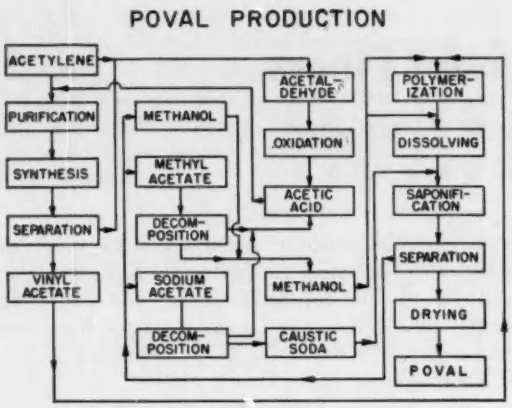

Fig. 1.

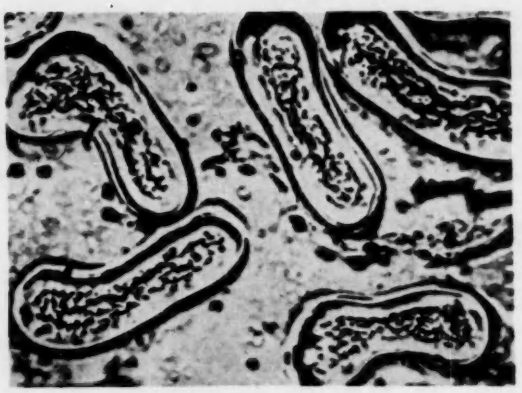

Fig. 3.

pattern of the fiber. This suggests that acetalization occurs only on the surface or in the amorphous interior portions of the filament. This view is supported by photomicrographs of filament cross sections (Figure 3). The degree of acetalization also affects the fiber. Higher molecular weight aldehydes have been used to improve the elasticity of the fiber. Vinylon of this type is expected to be introduced shortly. With some of the higher aldehydes, it makes no difference whether or not they are introduced before or after drawing and heat treatment. Other aldehydes, such as chloro-acetaldehyde, are used to facilitate introduction of amine or imine groups into the fiber.

When we attempt to evaluate the properties of vinylon, we must take into account the great varieties of the material that are available. There are, however, some general properties which apply to most grades currently produced. They have a specific gravity in water of 1.28 and an apparent specific gravity in air of 1.0 to 1.2. This places vinylon among the lightest of all fibers. The softening point of 220° C. is not far below that of the highest softening materials, 250° C. for wool and Orlon.[1] It has about three times the electrical resistance of cotton. It is insect-, mildew-, and fungus-resistant. Vinylon duck suffered little loss in strength after being immersed in water and then buried in earth much longer than the time required for complete decomposition of cotton duck. In both laboratory tests and actual wearing tests of vinylon garments (socks, underwear, etc.), it has shown an abrasion resistance and durability 5 to 20 times that of wool and 3 to 5 times that of cotton. Its thermal conductivity is much less than cotton and nearly as low as wool. While vinylon materials soil easily, they are not easily stained and are easy to wash and quick to dry.

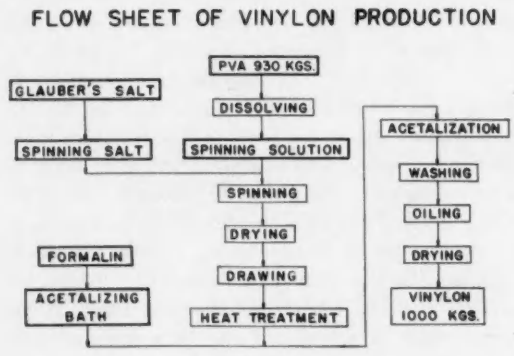

Fig. 2.

Although vinylon clothing has good crease retention, it wrinkles easily. This latter tendency is believed related to the low elasticity of the fiber. As this property is improved, wrinkle resistance should improve. At first appearances, the existence of numerous hydroxyl groups in the fiber should facilitate dyeing. However, these hydroxyl groups are apparently buried beneath the surface of the filament where it is difficult for the dye to penetrate. For this reason, brilliant hues are difficult to obtain. A large variety of dyes, however, is available for imparting pastel shades to vinylon material. The formation of amines and imines on the filaments was intended to improve the dyeability. This has not as

[1] Du Pont acrylic fiber.

yet been commercialized. Perhaps the most serious shortcoming of vinylon is the lack of wet-heat resistance. Originally the material shrank badly in boiling water. However, it will now stand up in water at approximately 120° C. with further improvements in sight. It is recommended that vinylon garments be dried before ironing.

The dry tenacity of vinylon fiber is compared with that of a number of others in Figure 4. No other fiber shows such a variation in tenacity or seems capable of such a high tenacity. As recently as three years ago, 3 g./den. was the highest tenacity yarn produced. Today, yarns with tenacities of 6 to 8 g./den. are common for industrial applications, while in the laboratory tenacities in excess of 10 g./den. have been achieved. The ratio of wet to dry tenacity, Figure 5, is comparable to that of most natural and cellulose-derived fibers but inferior to that of the synthetics. A comparison of the tenacity of vinylon with that of other fibers at several temperatures is shown in Figure 6. A similar comparison for prolonged heating at 150° C. is shown in Figure 7.

The relative resistance of vinylon to ultraviolet light is shown in Figures 8 and 9. Note that even under the relatively mild conditions of sunlight, the

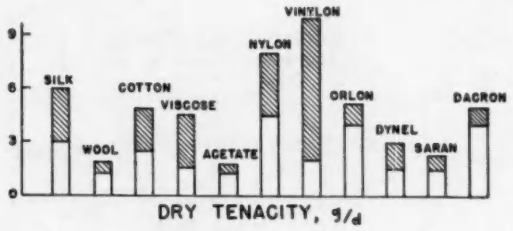

Fig. 4.

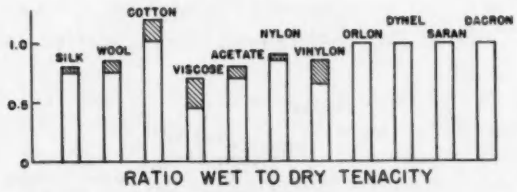

Fig. 5.

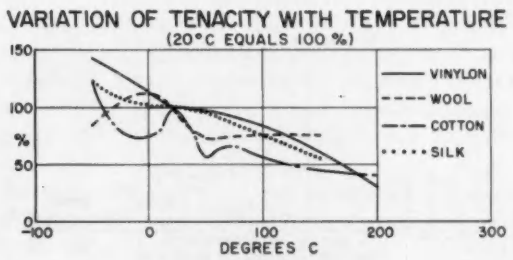

Fig. 6.

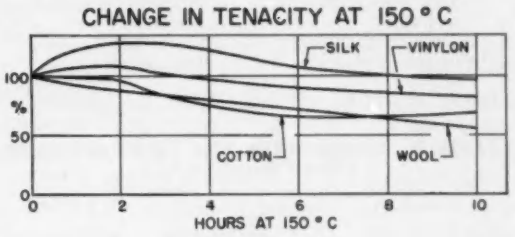

Fig. 7.

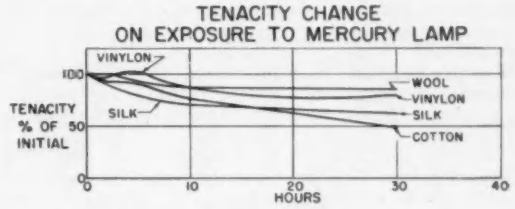

Fig. 8.

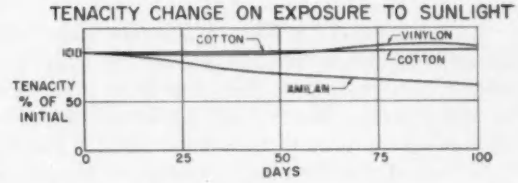

Fig. 9.

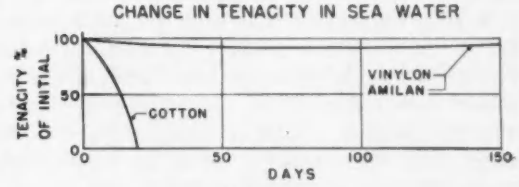

Fig. 10.

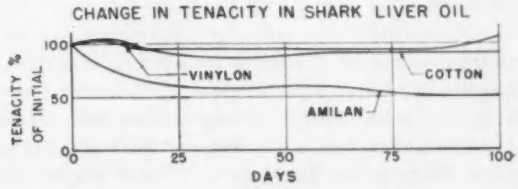

Fig. 11.

TABLE I. Substances That Produce No Change in Vinylon on Steeping 1 Hr. at Either 20° or 50° C.

Phosphoric acid, 15%	Ether
Glacial acetic acid	Acetaldehyde
Oxalic acid solution	Formamide
Butyric acid	Carbon tetrachloride
Glauber's salt, sat.	Carbon disulfide
Cupra-ammonium solution	Petroleum benzine
Pyridine	Petroleum
Methanol	Castor oil
Butanol	Mineral oil
Glycerine	

TABLE II. Substances That Affect Vinylon on Steeping 1 Hr. at Either 20° or 50° C.

Chemicals	20° C.	50° C.
Sulfuric acid, 35%	Slight swelling	Swelling
Sulfuric acid, 20%	No change	Slight swelling
Hydrochloric acid, 12%	No change	Dissolved, 15%
Nitric acid, 10%	No change	Weakens
Conc. phosphoric acid	Dissolved	—
Formic acid	Dissolved	—
Hydrogen peroxide	No change	Gelatinized
Caustic soda, 40%	No change	Yellowing
Formalin, 30%	No change	Gelatinized
Phenol	No change	Swelling
Cresol	No change	Shrank
Xylenol	No change	Shrank

polyamide, Amilan (a Japanese product), lost considerable strength.

The resistance of a fiber to both sea water and fish oils (Figures 10 and 11) is important when it is used in fish nets, tarpaulins, fish lines, and rope. Note that vinylon stood up well in both while cotton failed in sea water and the polyamide failed in fish oil.

In general, the chemical resistance of vinylon is excellent. Figure 12 shows that it loses but little strength when steeped in sulfuric acid ranging in concentrations up to 20%. Table I shows a partial list of chemicals that produce no change even at 50° C. It includes dilute and weak acids as well as a large variety of solvents. Of the reagents that do alter the material (Table II), only strong concentrated acids dissolve it. Even strong caustic soda merely discolors it. Other materials, formalin, hydrogen peroxide, and phenolics, tend to swell or shrink the fiber only.

A comparison of moisture regain and water absorption is shown in Figures 13 and 14. The moisture regain, being less than that of the natural and cellulose-derived fibers and higher than that of the synthetics, makes it one of the few hydrophilic synthetic fibers. This property is believed responsible for the comfortable wearing qualities of vinylon. It is reputedly warm in winter and cool in summer.

Some of the elastic properties of vinylon are compared in Figures 15 and 16. The commercial material currently produced has a very high modulus and, relative to nylon, a low elastic recovery—75 to 85% after a 2% stretch. As high elasticity and elastic recovery are important in some applications, highly elastic modifications of vinylon are expected to reach the Japanese market in the near future.

A comparison of the U.S. prices of several staples with the Japanese price of vinylon is given in Figure 17. The $0.70/lb. for vinylon is about twice the current price for cotton and the cheaper cellulosics. The price in the United States under comparable conditions would probably be slightly higher.

In view of the rapid advances toward reducing the price of vinylon, both in Japan and elsewhere, an accurate estimation of U.S. costs by the present process would seem valueless.

In 1949 the yield of vinylon based on acetylene was only 52% of theoretical. Yields are now approaching 70%, and this accounts in large measure

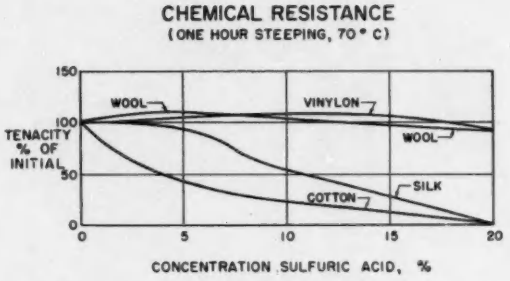

Fig. 12.

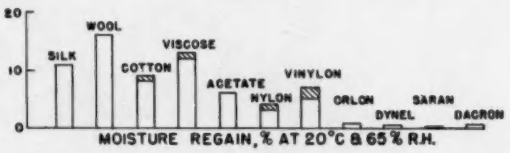

Fig. 13.

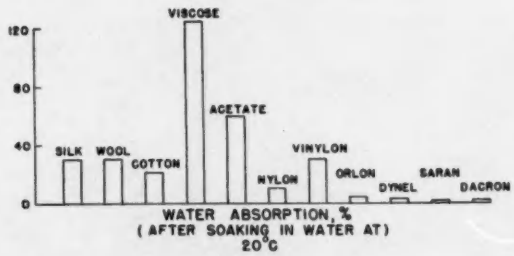

Fig. 14.

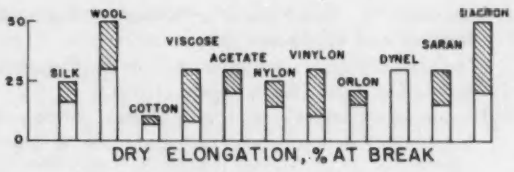

Fig. 15.

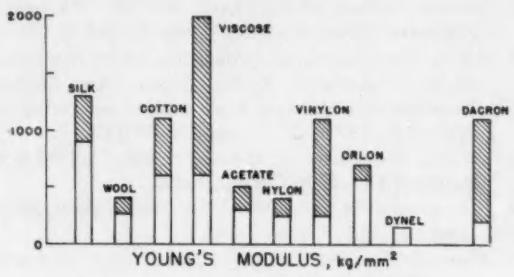

Fig. 16.

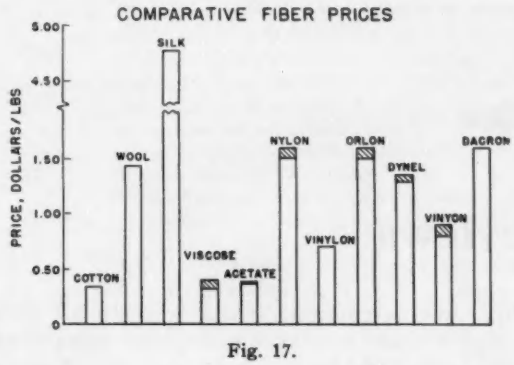

Fig. 17.

for the drop in price from the 1950 figure of $0.84/lb.

Another factor in the price is volume of production. Production prior to 1950 was only in development quantities. Production figures after that date rose from approximately 6,000,000 lb. each year in 1951 and 1952 to about 7,500,000 in 1953 and again in 1954. Production for 1955 was estimated at 20,000,000 lb. at the time of preparation of this report, with projected estimates of 30,000,000 to 35,000,000 for 1956 and 55,000,000 to 65,000,000 lb. for 1957. The more conservative estimate we have used still indicates the consumption of poval in Japan is rapidly approaching current U.S. production. Although these figures indicate enormous growth, they are still small when compared with other fibers. The largest vinylon plant produces less than 20 tons a day; the smallest, less than 2 tons. The entire current production would scarcely equal that of a single marginal rayon plant. In 1952 vinylon production represented only 3% of total synthetic fiber production, while the production of synthetic fibers bore a similar relationship to the entire fiber field. It is apparent that there is room for growth, and hence reduction in price well beyond present levels.

Plant integration is also another cost factor. At the present time Kurashiki Rayon Co., Ltd. is the only vinylon producer that also produces and controls the basic resin. All other companies, who divide less than half the business, obtain their polyvinyl alcohol from Nippon Synthetic Chemical.

One of the most important cost factors, however, (perhaps more important than expanded volume of production) is technological advancement. There is not a phase of the several production steps that is not receiving the closest scrutiny. Even the long-standing dream of the resin chemist: to combine acetylene and water more directly into polyvinyl alcohol (which by a devious route is essentially what is done) is receiving at least some consideration. In view of this effort, a major technical breakthrough should not be unexpected.

Thus we see that from the standpoint of technology, the Japanese are attempting to develop an extremely versatile fiber that, in its various modifications, will serve in virtually every textile application. From the standpoint of economics, their purpose is much more simple and clear-cut. They want to reduce the price of vinylon to a point where it will compete with cotton and the cellulosics. They face both these problems with confidence, an optimism that seems to be shared by the Germans.

Vinylon, in all of its presently produced forms, is far from being the perfect all-purpose fiber. Yet, no other fiber, natural or synthetic, comes so close. No other commercially produced fiber can be subjected to such great variation or hold forth the possibility of still greater improvement. It seems destined for an accelerated expansion in Japan and early industrialization in Germany. As for its future elsewhere, we can do no better than quote the words of T. Tomonari:

"It is said, for instance, that production of cotton, wool, and silk is competing with production of foodstuffs, and has, therefore, reached the limit of its expansion. The situation can rightly be considered to work in favor of development of man-made fibers. While on the other hand, cellulosic man-made fibers are faced with impending exhaustion of forests

throughout the world and thus the speed of expansion and development was naturally checked, calling for an expansion of noncellulosic man-made fibers, expansion of some types of synthetic fibers may also be limited by scarcity of their basic natural resources. The main natural resources for vinylon are coal, petroleum or natural gas and electricity and fuel. Therefore, throughout the world, vinylon production can be expected to be undertaken wherever coal, petroleum or natural gas and electricity are available in order to meet the increasing demand of the world for textile fibers. A broad horizon looms ahead for vinylon."

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3. *What Is "Kuralon" and How to Use It,* Kurashiki Rayon Co., Ltd., Osaka, Japan (1955).
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* With the exception noted, apparently none of our Japanese references have been published in periodicals.

Manuscript received December 5, 1955.

Book Reviews

The Mechanical Characters of Jute. K. R. Sen. Calcutta, India, India Central Jute Committee, 1954. 36 pages. Price, 35 cents.

Reviewed by S. J. Hayes, Ludlow Manufacturing Co., Needham Heights, Mass.

The article purports to review 15 years of research at the Research Laboratories of the Committee. The literature cited are mostly Indian publications available in extremely few American libraries.

The author points out that successful manufacture of jute products involves reduction of slubs and hairiness and production of smooth fine yarns with minimum wastage. Fiber should be chosen having low frictional resistance at the filament surface and a low average complexity. In blends, the components should have similar linear densities of filament. Slubs are avoided by reducing the proportion of fiber shorter than 10 cm. (4 in.). It is conceded that these prerequisites cannot be controlled from direct a priori knowledge. Hairiness arises from fiber with high linear density and high Young's modulus and from too tight or too slack twist.

Preparing should yield mostly single filaments with the least possible cross-section area, and nearly circular in section. The intrinsic material strength should be high; the complexity modulus should be low; and torsional modulus should be low. Stock preferably should cure a week or ten days after batching.

Filament hardness varies among different jutes under the same batching conditions. Hence the oil-water proportion and the amount of application should be established for each parcel of jute before use. Twisting sets up strains in yarn. The strain can be released and twist "set" by wetting and then drying the yarn. An agreed standard for comparing spinning values of jutes is needed, because various jutes act differently in 4-lb, 10-lb, and 40-lb yarns. Hardness estimation, a factor devised by the author

and measured on an instrument of his own invention, is advocated as the best guide to the effect of chemical and physical treatments on jute.

A list of 12 physical characteristics is cited as defining jutes. All are measured by methods developed by the author, and eight of them are published in obscure Indian journals.

Practically all of the conclusions confirm general empirical knowledge which the industry has long had, or which is available in general scientific literature. No indication is given of how these desiderata may be implemented.

The author disregards the physical limitations of time and space that preclude the niceties of fiber selection, of blending, and of ripening or batching which he advocates.

The problem reduces to the old question: Who will bell the cat?

GORDON RESEARCH CONFERENCES, AAAS

11 June—31 August, 1956

The Gordon Research Conferences of the American Association for the Advancement of Science for 1956 will be held from 11 June to 31 August at Colby Junior College, New London, New Hampshire; New Hampton School, New Hampton, New Hampshire; and Kimball Union Academy, Meriden, New Hampshire.

Individuals interested in attending the Conference are requested to send in their applications to the Director. Each applicant must state the institution or company with which he is connected and the type of work in which he is most interested. Attendance at each Conference is limited to 100.

Requests for attendance at the Conferences, or for any additional information should be addressed to W. George Parks, Director, Department of Chemistry, University of Rhode Island, Kingston, Rhode Island. From June 11 to August 31, 1956 mail should be addressed to Colby Junior College, New London, New Hampshire.

	Colby Junior College New London, N. H.	New Hampton School New Hampton, N. H.	Kimball Union Academy Meriden, N. H.
11–15 June	Catalysis	Organic Reactions and Processes	Lipids
18–22 June	Petroleum	Metals at High Temperatures	Stream Sanitation
25–29 June	Separation and Purification	Proteins and Nucleic Acids	Nuclear Chemistry
2–6 July	Polymers	Coal	Chemistry and Physics of Isotopes
9–13 July	Textiles	Radiation Chemistry	Solid State Studies in Ceramics
16–20 July	Corrosion	Organic Coatings	Bones and Teeth
23–27 July	Instrumentation	Chemistry and Physics of Metals	Chemistry at Interfaces
30 July–3 Aug.	Elastomers	Steroids and Related Natural Products	Ion Exchange
6–10 Aug.	Food and Nutrition	Analytical Chemistry	High Pressure Research
13–17 Aug.	Vitamins and Metabolism	Inorganic Chemistry	Toxicology and Safety Evaluations
20–24 Aug.	Medicinal Chemistry	Statistics in Chemistry and Chemical Engineering	Infra-Red Spectroscopy
27–31 Aug.	Cancer	Adhesion	Glass

TEXTILE CONFERENCE

Colby Junior College, New London, N. H., 9–13 July 1956

G. R. Seidel, *Chairman*

H. A. Secrist, *Vice-Chairman*

Monday 9 July	"Some Recent Advances in the Chemical Transformation of Cotton into New Fibers" Wilson A. Reeves and William Weaver, Southern Regional Research Branch, U.S.D.A.
	"Electrostatic Properties of Finished Cellulose Acetate Yarns" G. J. M. Sprokel, American Viscose Corp.
Tuesday 10 July	"Chemical Modifications of Wool as Related to Fiber Properties" Milton Harris and Robert Saxon, Harris Research Laboratories, Inc.
	"Textured Filament Yarns" L. G. Ray, E. I. du Pont de Nemours & Co., Inc.
Wednesday 11 July	"New Polymers as Potential Fiber Formers" Herman Mark, Polytechnic Institute of Brooklyn
	Subject to be announced W. Weltzein, Krefeld, Germany
Thursday 12 July	"Dimensional Effects in Measurement of Textile Properties" Stanley Backer, Massachusetts Institute of Technology
	"Glass Textile Sizes and Finishes" Alfred Marzocchi and J. K. Park, Owens-Corning Fiberglas Corp.
Friday 13 July	"Wool Fiber Shape Factors: Effect on Fiber Properties, Processing Behavior and Fabric Properties" John Menkart, Textile Research Institute